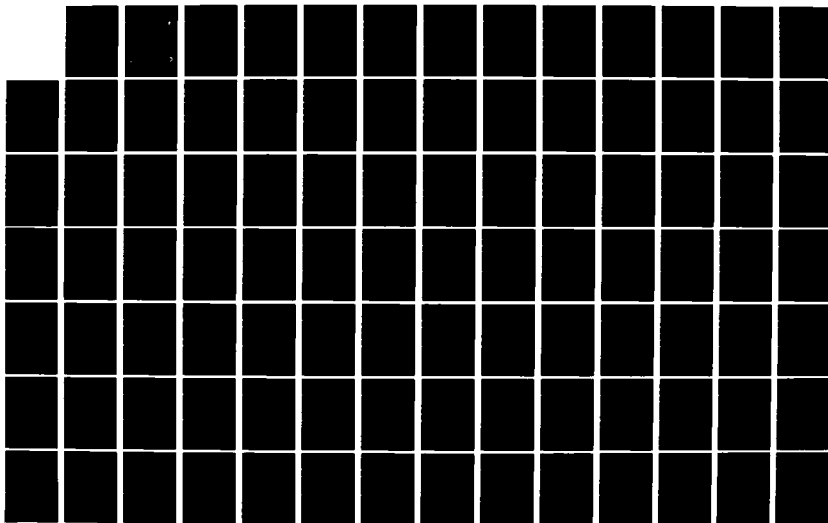


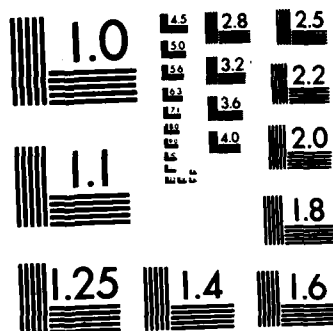
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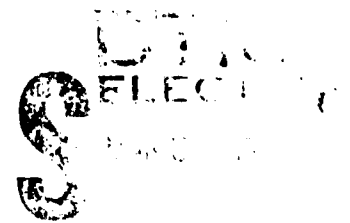
ANNUAL TECHNICAL REPORT
MATERIALS RESEARCH LABORATORY

Brown University
Providence, RI 02912

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PREFACE

The Materials Research Laboratory at Brown University is engaged in interdisciplinary research directed toward the solution of problems in various areas of Materials Science.

In this report, Sections I-IV represent major thrust areas; the remaining sections are less extensive, since they cover either new areas of activity, emerging thrusts with a smaller number of investigators, or derive their principal funding from sources other than the NSF-MRL program.

Although the research summaries in this report are contributions from individual investigators, introductions to the four major thrust area summaries have been provided by investigators who during the reporting period assumed the functions of coordinators of those thrust areas. These are: Plasticity of Solids, R.J. Clifton; Fracture of Solids, L.B. Freund; Inorganic Glasses, W.M. Risen, Jr.; and Solid Surfaces, P.J. Estrup.

Since many of the research areas are interrelated, cross references have been made when the work might, with equal justice, have been placed in two or more sections.

The largest single source of support for this Laboratory is the Materials Science Branch of the National Science Foundation. Substantial support also came from twenty other agencies, and of course, Brown University.

The Materials Research Laboratory at Brown University is administered by a Director, an Associate Director, and a committee composed of faculty members in representative areas of Materials Science.

The present appointees are:

Director:	G.S. Heller
Associate Director:	W.M. Risen, Jr.
Advisory Committee:	R.H. Cole L.N. Cooper P.J. Estrup R.J. Clifton J. Tauc

Those presently assuming the role of thrust area coordinators are:

Plasticity of Solids:	R.J. Clifton
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Fracture of Solids:

L.B. Freund

Inorganic Glasses:

W.M. Risen, Jr.

Solid Surfaces:

P.J. Estrup

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SECTION 1

Plasticity of Solids

Introduction

Research in this thrust area is directed towards improved understanding of the mechanisms of plastic deformation. High strain rate plastic response and strain localization are areas of continuing interest. Developing interests include martensitic transformations and the plastic response of steels. Other plasticity research related directly to ductile fracture is reported under the Fracture of Solids thrust.

Strain rate and strain rate history effects have been examined over the range of strain rates from 10^{-4}s^{-1} to 10^5s^{-1} by using a combination of techniques. At the higher strain rates the range of $10^2 - 10^3\text{s}^{-1}$ is covered by using the torsional Kolsky bar technique (Duffy) and the range from $10^4 - 10^5\text{s}^{-1}$ is covered by using pressure-shear plate impact experiments (Clifton). Dynamic torsion experiments on high purity aluminum single crystals show a marked increase in strain rate sensitivity of the flow stress at strain rates greater than 500s^{-1} . Dislocation cell walls have been observed by transmission electron microscopy. The flow stress and the strain rate sensitivity increase with decreasing cell size (Duffy, Chiem). In the pressure-shear experiments investigations of the response of aluminum, copper, and α -titanium have been completed (Clifton, Li, Gilat). Preliminary experiments have been conducted on adapting the pressure-shear configuration for measuring the flow stress of high strength steels.

Shear bands attributed to thermoplastic instabilities have been investigated experimentally and theoretically. Experimental investigations have been directed towards the development of a means for monitoring the temperature in and near a developing shear band (Duffy). Analytical investigations have addressed the comparison of linear stability analysis with computer simulation for studying instabilities in pure shear (Clifton, Molinari).

Investigations of dislocation dynamics in single crystals have included direct dislocation velocity measurements in Fe-3% Si crystals subjected to submicrosecond pulses (Clifton, Kumar). Related dislocation dynamic studies on LiF crystals includes further study of the effects of surface damage on precursor decay (Clifton, Meir) and the

effect of large amplitude, long duration bias stress pulses on ultrasonic attenuation (Elbaum, Hikata). The latter investigation shows that the peak attenuation occurs after the peak amplitude of the stress pulse.

An investigation of the kinematics of martensitic transformations has led to a simple characterization of the arrangement of phase boundaries and the discontinuities that occur across these boundaries (James). A stable solution of a boundary-value problem for neighboring regions occupied by coherent phases has been found.

A metal matrix composite with short metal fibers has been tested in a dynamic cantilever beam experiment to determine its dynamic plastic response (Kolsky). Although basic features of the response are compatible with predictions of a theory for inextensible fibers it appears necessary to include fiber extensibility to obtain satisfactory agreement between theory and experiment.

SECTION 1

Plasticity of Solids

Individual Contributions

Strain Rate and Strain Rate History Effects During Plastic Deformation

The overall goal of this research is to provide a better understanding of the mechanical response of structural metals subjected to dynamic loading. Our approach is to study material behavior through experiments in which specimens are subjected to quasi-static, dynamic and incremental strain rate loading well beyond the elastic limit. Included in the experiments are the effects of temperature and loading history. Our experimental techniques include microscopic as well as macroscopic studies of test materials, which range from alloy steels to monocrystals of aluminum and lithium fluoride. This work is closely related to that of Professor R.J. Clifton who attains strain rates considerably higher than ours. While we cover the strain rate range 10^{-4} s^{-1} to 10^3 s^{-1} , his experiments are in the strain rate range of 10^4 s^{-1} to 10^5 s^{-1} . Thus our combined experiments can determine the dynamic properties up to 10^5 s^{-1} on specimens of the same material.

Our most recent work has involved high purity aluminum single crystals deformed in shear at strain rates in the range $4 \times 10^{-5} \text{ s}^{-1}$ to 1600 s^{-1} . The shear traction is applied on planes parallel to a preferred slip system. Constant as well as incremental strain rate experiments were conducted. The results of the macroscopic tests show that the strain rate sensitivity in crystals of high purity aluminum is quite high. Furthermore, while the flow stress can be represented approximately by a linear function of the logarithm of strain rate up to strain rates of 500 s^{-1} , for larger strain rates it increases more rapidly. This change in behavior in the neighborhood of 500 s^{-1} is pronounced enough to imply a change in the dominant dislocation mechanism of dynamic deformation. Strain rate history effects due to the quasi-static prestrain appear qualitatively similar to those observed in polycrystalline aluminum, except that they are not erased by continued dynamic straining after the increment in strain rate unless the amount of quasi-static prestrain is small. For the microscopic investigation, use was made of transmission electron microscopy. It revealed that dislocations form

cell-like subgrains as the strain accumulates. These cells are considerably smaller after dynamic straining than after quasi-static straining. Furthermore, it appears that the flow stress varies inversely with cell size, although not necessarily in accordance with the Hall-Petch relation. The strain rate sensitivity also depends on cell size and varies inversely with its square.

Other current work includes a study of the effect of strain rate history and temperature history on flow stress in polycrystalline steel and aluminum. In these experiments, either a strain rate increment or a temperature decrement is imposed during torsional deformation of tubular specimens at the quasi-static strain rate of $5 \times 10^{-4} \text{ s}^{-1}$. In most metals, for instance in fcc and hcp metals, the flow stress for a given strain is lower if the metal has first undergone a quasi-static prestrain. For mild steel under the proper temperature conditions, however, it appears that the opposite is the case: the dynamic flow stress after a static prestrain overshoots that found by straining entirely at the dynamic rate. The amount of this overshoot depends on specimen temperature, becoming progressively more pronounced at lower temperatures. This contrast between the behavior of steel and that of aluminum as regards strain rate history seems to have a parallel for temperature history. Imposing a sudden drop in the test temperature during the deformation of steel raises the subsequent flow stress to a value greater than found in deformation entirely at the lower temperature, whereas for aluminum a drop in temperature raises the flow stress only to a value considerably less than obtained in a test conducted entirely at the lower temperature. This difference in the behavior of steel and aluminum will be investigated further by means of TEM observation of the specimens.

Finally, we are investigating the causes of shear banding in steel specimens subjected to dynamic loading. Shear bands have important applications, as in penetration or in machining, and frequently precede fracture. In our tests, we have developed a technique for monitoring the temperature profile within and to either side of a shear band as it forms in a thin-walled tubular steel specimen. For this purpose we use a linear array of infrared radiation detectors, each of which measures temperature over an area with a 0.02 inch diameter. Thus far we have successfully applied the technique to establish the temperature profile at five points along the gage length (0.1 inch) of 1018 CRS steel specimens during straining at 10^3 s^{-1} .

Principal Investigator: J. Duffy (Engineering).

Personnel: R.H. Hawley (Engineering), G.J. LaBonte, Jr.

(Engineering), P. Rush (Engineering), K.A. Hartley (Engineering), A.A. Morrone (Engineering).

Publications: "Strain Rate History Effects in Body-Centered-Cubic Metals," J. Klepaczko and J. Duffy, Proceedings Conference on Mechanical Testing for Deformation Model Development, ASTM STP 765, R.W. Rohde and J.C. Swearingen, Eds., ASTM 1982, 251-268.

"Strain Rate History Effects and Observations of Dislocation Substructure in Aluminum Single Crystals Following Dynamic Deformation," C.Y. Chiem and J. Duffy, MEA 79-23742/3, MRL E-137, October 1981, to appear in Materials Science and Engineering.

"Dynamic Deformation of Mono and Polycrystalline Specimens Using the Kolsky Bar", Proc. 18th Annual Meeting of the Society of Engineering Science, Brown University, Providence, RI (September 1981).

"History Effects in Polycrystalline BCC Metals and Steel Subjected to Rapid Changes in Strain Rate and Temperature," J. Klepaczko and J. Duffy, DMR 79-23257/141, NSF CME79-23742/5, June 1982, to appear in Archives of Mechanics, Warsaw, Poland, 4 (1982).

Supported by the Materials Research Laboratory/NSF, the Army Research Office, and the National Science Foundation.

Pressure-Shear Plate Impact Experiments

Two types of pressure-shear experiments are being conducted. In one, thin specimens (0.2-0.4mm thick) are sandwiched between two elastic plates in order to obtain sustained plastic shear strain rates of approximately 10^5 s^{-1} . In the other, two plates of the same material are impacted and the wave profiles produced are used to study the plastic response of the materials. Theses on both types of experiments were completed during the year.

New development in pressure-shear experiments has been directed towards extending the range of applicability of these experiments to include investigations of the plastic response of high strength steels. Preliminary experiments with 4340 steel specimens sandwiched between tungsten carbide plates resulted in yielding of the tungsten carbide plates. Recent experiments suggest that very high strength steel plates can be used as elastic anvil and flyer plates

for studying the plastic response of many reasonably high strength steels.

Principal Investigator: R.J. Clifton (Engineering).

Personnel: C. H. Li (Engineering), Al Gilat (Engineering), R. Klopp (Engineering), L. Hermann (Engineering) and R. M. Reed (Engineering).

Publications: "A Pressure-shear Experiment for Studying the Dynamic Plastic Response of Metals at Shear Strain Rates of 10^5 s^{-1} ," C. H. Li, Ph.D. thesis, Brown University, December 1981.

"An Experimental and Numerical Investigation of Pressure-shear Waves in 6061-T6 Aluminum and Alpha-titanium," A. Gilat, Ph.D. thesis, Brown University, August 1982.

Supported by the Materials Research Laboratory/NSF, the National Science Foundation, and the Army Research Office.

Thermal Viscoplastic Instability in Shear

Simple shear has been investigated for materials which exhibit viscoplasticity, thermal softening (or hardening), strain hardening, thermal conductivity, and elasticity. Quasi-static and dynamic deformations have been considered. Numerical solutions to the fully nonlinear system of governing equations have been compared with analytical solutions of linear equations obtained by neglecting higher order terms in differences from a homogeneous solution. Solutions of the linearized equations agree with the numerical solutions of the nonlinear equations for early times following the introduction of a small perturbation. However, the solutions of the linear perturbation problem are not reliable indicators of the late-time stability of the deformation.

Principal Investigator: R.J. Clifton (Engineering).

Personnel: A. Molinari (Engineering) and T. Shawki (Engineering).

Supported by the Materials Research Laboratory/NSF and the Army Research Office.

Dynamics of Dislocations in Single Crystals

Single crystals of high purity LiF with damage-free, flat surfaces have been impacted in order to study the effect of surface damage on the decay of the elastic precursor. Specimens have been placed between two fluid layers to eliminate damage due to impact of rough surfaces. Chemical polishing with high purity distilled water has been used to obtain surfaces at which the dislocation density is the same as the bulk dislocation density--approximately $5 \times 10^4 \text{ cm}^{-2}$. Precursor amplitudes are smaller than predicted by considering the precursor decay associated with the initial dislocation density and neglecting the effects of nonlinear elasticity. Decay of the precursor over the distance between 3 and 6 mm from the impact end is small--comparable to the error band for the experiments. The wave profile behind the precursor decays strongly over this distance. Nonlinear elasticity effects on precursor decay are being examined.

Dislocation mobility in Fe-3%Si single crystals has been studied by means of plate impact experiments. In these experiments the crystals are subjected to 200-400 ns stress pulses and the crystals are examined afterwards to determine distances moved by dislocations during the pulse. Dislocation motion is observed on many slip systems. Because of the variety of slip systems that are activated and the differences in resolved shear stresses on these systems, each experiment provides much information on dislocation mobility. Such dislocation mobility studies in bcc metals appear to be particularly promising and are being continued.

Principal Investigator: R. J. Clifton (Engineering).

Personnel: P. Kumar (Engineering) and G. Meir (Engineering).

Publication: "Surface Damage Effects on Precursor Decay in High Purity LiF," G. Meir, Sc.M. thesis, Brown University, May 1982.

Supported by the Materials Research Laboratory/NSF and the National Science Foundation.

Ultrasonic Studies of Deformation Under Stress-Pulse Loading

We have previously described results obtained on stress-pulse loading through the use of ultrasonic measurements. In these studies a system constructed here is used to record ultrasonic attenuation and velocity changes at ~ 10 microsecond intervals, while a stress pulse of ~ 100 microsecond duration is applied. In particular, we observed that the maximum of the stress pulse is reached before that of the ultrasonic attenuation change.

In order to account for these and related results on ultrasonic velocity changes, we developed a model for time-dependent motion of dislocations under the conditions of our experiments. We have obtained qualitative agreement between the model predictions and the experiments. Additional measurements will be carried out to determine the extent of quantitative agreement.

Principal Investigator: C. Elbaum (Physics).

Personnel: A. Hikata (Applied Mathematics).

Supported by the Materials Research Laboratory.

Mechanics of Martensitic Transformations

We have begun a program of research on coherent phase transformations in solids which accounts for the three-dimensional changes of shape occurring in a body. The framework is sufficiently general to describe the simplest stress-induced transformations in a realistic kinematic setting. No change of composition is allowed.

We began with a study of the kinematics of martensitic transformations. When several variants of a martensitic phase meet at a point in a body, we found that a mild assumption of coherence, applicable to transformations involving finite strain discontinuities, places strong restrictions on the way these phases arrange themselves. A classification was developed based upon the number of interfaces present. Curiously, many of the simplest arrangements have the property that their amplitudes are parallel, the amplitude being a vector attached to each

interface similar to amplitudes defined in studies of the propagation of shock waves. The implications of this fact for volume changes and stress fields were studied. The classification should be useful to geologists who wish to decide if an observed transformation occurred by diffusion and growth at high temperatures or by the application of force at low temperatures; we also foresee applications to the joining of materials and the structure of domains in ferroelectric materials.

We have found what we think is the first stable solution of a boundary-value problem having regions occupied by coherent phases. The boundary conditions permit non-hydrostatic tractions, and the regions occupied by the phases need not be parallel plates. This should provide a background for calculations of the effect of applied forces upon transformation temperatures, and a way to assess the role of metastability in solid-state transformations.

We plan further research on transformations in which there is a change of composition.

Principal Investigator: Richard D. James (Engineering).

Personnel: M.M. Ramazanoglu (Engineering).

Publications: "Mechanics of Coherent Phase Transformations in Solids", R.D. James, Brown University Technical Report, October 1982.

Supported by the Materials Research Laboratory /NSF and the National Science Foundation.

The Mechanical Response of Fiber Reinforced Materials

Experiments have been carried out on the mechanical response of composite metal cantilevers to dynamic transverse impacts. The impacts were produced in a 'Hyge' shock testing machine and the durations of the impacts were of the order of one millisecond. The cantilever specimens were fabricated by embedding stiff wires (steel piano wires and phosphor bronze wires) in a soft metal substrate (lead or lead-tin alloy). The wires were all oriented parallel to the axes of the cantilevers. Since the yield strength of the reinforcing wires is many times greater than that of the surrounding metal substrate, when yield occurs it is in the form of plastic-shear of the soft substrate. The nature of

the observed deformations has been shown to be in general agreement with the theoretical predictions of Spencer and his co-workers. These predictions were based on the model of ideal reinforced composites made up of inextensible fibers embedded in an incompressible substrate with a sharp yield point. The deviations which have been found between the observed behavior and that predicted by Spencer, are attributed to the finite extensibility of the reinforcing fibers and efforts are at present being made to modify the model to allow for this effect.

Reference: "Dynamics of Ideal Fiber Reinforced Rigid Plastic Beams". A.J.M. Spencer, J. Mech. Phys. Soc. 22 (1974), 147.

Principal Investigator: H. Kolsky (Applied Mathematics).

Personnel: J. Mosquera (Engineering), G. Sun (Applied Mathematics), W. Carey (Applied Mathematics), P. Russo (Applied Mathematics).

Publications: "Dynamic Loading of Fiber Reinforced Beams", H. Kolsky and J.M. Mosquera, to appear in Mechanics of Material Behavior, Elsevier, Amsterdam (1983).

Supported by the Materials Research Laboratory/NSF, and N.S.F.

SECTION 2

Fracture of Solids

Introduction

The research goals of the Fracture of Solids Group are (i) a comprehensive understanding of the influence of material microstructure and microscale mechanisms on the macroscopic fracture response of materials; and (ii) the characterization of the resistance to fracture initiation and crack propagation in materials. Summaries of work completed during the reporting period on a range of experimental and theoretical topics concerned with the fracture of metals and alloys, as well as with polymers and ceramics, are presented in this section. A total of nine faculty members from the Materials Science Group and the Mechanics of Solids Group, both within the Division of Engineering, and from the Division of Applied Mathematics contributed to work in this thrust area during the year. A number of graduate assistants, research associates, and research staff members were also involved.

Progress has been made on correlation of microstructure with fracture toughness in steels. Work has focused on high strength steels, principally quenched and tempered 4340 steels. A good correlation has emerged between the size and spacing of carbides and fracture initiation resistance (Asaro). The correlation is based, in part, on a theoretical analysis of ductile void growth and coalescence by strain localization in the crack tip region (Needleman, Asaro). A test technique based on the circumferentially notched round bar has been developed for inducing fracture in structural steels over six orders of magnitude in loading rate (Duffy), and work has begun on the systematic identification of micromechanisms of fracture initiation in 1020 hot rolled steel. In other work on two-phase materials, the microstructure of a sintered WC-Co has been characterized and correlated, through a theoretical plastic slip line analysis, to deformation and fracture response of the material (Gurland). Similar work has been completed for dual phase steels with approximately 15 volume percent of martensite (Gurland).

At the level of macroscopic fracture response, an area of emphasis has been the study of the mechanics of crack growth in materials, including the effects of nonlinear response and inertia. In a theoretical study of dynamic elastic-plastic crack growth, it has been shown that material

inertia on the microscale can have a major influence on the observed dependence of dynamic fracture toughness on crack propagation speed, and some limitations of asymptotic crack tip solutions in dynamic elastic-plastic fracture mechanics have been pointed out (Freund). In a parallel experimental study, the dependence of dynamic fracture toughness on crack propagation speed during rapid fracture of single edge notched 4340 steel specimens has been determined by means of the optical shadow spot method (Duffy, Freund). The theoretical basis for extending this method, which has been applicable only in situations with small scale yielding, has been established (Freund).

Research on inhomogeneous plastic deformation and strain localization, viewed as a precursor to ductile fracture, has been pursued jointly with the Plasticity of Solids thrust area. Theoretical work has continued on plastic strain localization in the highly deformed crack tip region in ductile materials due to yield surface vertex formation or microvoid formation, and an experimental study on notched bend specimens with variable notch root radii has been initiated (Asaro, Needleman). Significant progress has also been made in the analysis of inhomogeneous elastic-plastic deformation of single crystals with pronounced latent hardening and strain rate sensitivity (Needleman, Asaro).

A variety of other projects have been carried out, including a combined analytical and experimental study of the fracture of brittle fiber-reinforced composite materials, such as fiber-glass composites (Kolsky, Pipkin); oxidation and fracture resistance of reaction bounded silicon nitride (Richman); and numerical analysis of fracture specimens exhibiting viscoplastic material response (Shih).

Section 2

Fracture of Solids

Individual Contributions

The Fracture of Fiber-Reinforced Composites

Both theoretical and experimental work on propagation of brittle cracks through specimens of fiberglass composites (Scotchply 1002) has continued. Since the tensile strength of the reinforcing glass fibers is considerably greater than that of the epoxy substrate brittle fractures are generally found to propagate through the substrate rather than across the fibers. When, however, cantilever specimens made of crossply fiberglass with one set of fibers parallel to the axis of the cantilever and the other orthogonal to the fiber axis, are subjected to transverse loads the fracture is found to propagate either parallel to the axis of the cantilever or perpendicular to it. This is to be expected since under these conditions both families of fibers are in a state of tension and the direction the crack chooses depends on which set of fibers are first subjected to tensile stress greater than their tensile strengths. It is found that, in general, the fracture starts by running parallel to the axis of the cantilever and then suddenly changes its direction by 90° and runs parallel to the applied tensile stress until it reaches the edge of the specimen. The theory of this behavior has been shown to correspond to predictions based on the model of an ideal fiber reinforced solid, where it is assumed that the fibers are completely inextensible so all deformations which occur must be in the form of shear. The predictions of this theory are in reasonable agreement with the observed behavior and a paper has been published describing the experiments and the theory (Sun, Kolsky, and Pipkin). Some very clear deviations between theory and experiment have, however, been observed and these are attributed to the finite extensibility of the glass fibers so that some bending as well as shear takes place. A paper is being prepared which includes this correction.

Principal Investigator: H. Kolsky (Applied Mathematics).

Personnel: G. Sun (Applied Mathematics), P. Russo (Applied Mathematics), W. Carey (Applied Mathematics).

Publication: "An Experimental and Theoretical Study of Crack Propagation in Crossply Fiber Composites", G. Sun, H. Kolsky and A.C. Pipkin, in press, J. Engineering Mechanics (1982).

Supported by the Materials Research Laboratory/NSF.

Failure of Fiber-Reinforced Materials

In research experiments by Sun and Kolsky (q.v.), plates of fiberglass-epoxy composite were cut with edges parallel to the two families of fibers, a crack was started with an edge notch, and it was then extended by applying a load quasi-statically in the direction perpendicular to the crack. It was observed that after growing parallel to one family of fibers for some distance, the crack would turn through a right angle and run toward the nearest edge of the plate, parallel to the second family of fibers. This agrees with predictions based on the assumption that fiber extensibility can be neglected. According to the theory, the length of the crack at the point where it turns depends sensitively on its distance from the edge, with cracks closer to the edge turning sooner. The experimental results are in qualitative agreement with this prediction. Quantitative agreement is fair but not exact.

Principal Investigator: Allen C. Pipkin (Applied Mathematics).

Publications: "An Experimental and Theoretical Study of Crack Propagation in Crossply Fiber Composites", G. Sun, H. Kolsky, and A.C. Pipkin, Engng. Fracture Mech., 16, forthcoming.

"Cracks in Inextensible Materials", A.C. Pipkin, Proc. 9th U.S. National Congress of Appl. Mech., 1982 (forthcoming).

Supported by the Materials Research Laboratory/NSF.

Microstructure and Fracture Toughness of Cemented Carbides

A study was completed of the microstructural development taking place during liquid phase sintering of WC-Co alloys. Special attention was given to the structure of WC boundaries which are known to play an important role in the plasticity and fracture of these alloys.

In this investigation, the orientation relationship between contiguous carbide particles was established on the equilibrated microstructure using the slip line method. The theoretical interpretation of these results is based on the crystallographic structure of the grain boundaries, as described by the Coincidence Site Lattice (CSL) model. The results indicate that the large, well developed crystals in an equilibrated structure adhere preferentially in a high coincidence lattice orientation.

The extent of carbide-carbide contacts and the development of the skeleton structure of the WC phase during sintering was measured in terms of continuity, contiguity and grain growth. This study suggests that, in the initial stages of sintering, liquid cobalt penetrates preferentially the high energy boundaries. During continued sintering, the further reduction in contiguity is a consequence of the geometrical effects of grain growth and not necessarily the continued penetration of WC-WC boundaries.

Principal Investigator: J. Gurland (Engineering).

Personnel: R. Deshmukh (Engineering) and H. Stanton (Engineering).

Publications: "Deformation and Fracture of Sintered WC-Co Alloys", J. Hong and J. Gurland, Proc. Int. Conf. on Science of Hard Materials, Jackson, Wyoming (1981), Pergamon Press, New York, N.Y., (1982).

"A Study of Liquid Phase Sintering and Micromorphology of WC-Co Alloys", R.D. Deshmukh, Ph.D. thesis, (J. Gurland, sponsor), Brown University, June 1982.

"The Orientation of Contiguous Tungsten Carbide Crystals in Sintered WC-Co as Determined from Slip Line Traces", R. Deshmukh and J. Gurland, Metallography, 15 (1982), No. 4.

Supported by the Materials Research Laboratory/NSF.

Strength and Fracture of Two-Phase Alloys

Dual-Phase steels contain 15-20 volume percent of martensite and 80-85 percent of ferrite. An attempt was made to estimate the load transfer between ferrite and martensite in the plastic range by adapting to irregular particles a shear lag model similar to that used for discontinuous uniform fibers. It was shown that the ratio of the stresses carried by martensite and ferrite is proportional to the average aspect ratio of the martensite particles. The calculated stress ratio is in fair agreement with that measured at low strain by the Bauschinger effect, as cited in the literature. It leads to the prediction of martensite yielding at the high strains corresponding to necking in ferrite deformation, in agreement with the observed results previously reported.

In a typical dual-phase steel, the martensite carries approximately 30% of the load while occupying only 15% of the volume. These results show that the stress carried by the martensite could significantly affect the strength of the alloy, and must be taken into consideration for the purposes of alloy design.

Principal Investigator: J. Gurland (Engineering).

Personnel: H. Stanton (Engineering) and Y.L. Su (Engineering).

Publications: "A Study of the Deformation and Fracture of a Dual-Phase Steel", A.F. Szewczyk and J. Gurland, Metallurgical Transactions, 13A (1982), No. 10.

Supported by the U.S. Department of Energy.

Analysis of Dynamic Crack Growth in Elastic-Plastic Materials

The study of the effects of inertia during elastic-plastic crack growth has been continued. During this year, a numerical study of steady-state antiplane shear crack growth in a rate-sensitive material has been carried out. The analysis is based on continuum mechanics, and the material

is modeled as being elastic-viscoplastic. Using the small scale yielding concept of fracture mechanics and allowing only for steady state crack growth, but including the effects of material inertia explicitly, a full field solution for the deformations is obtained by means of an iterative procedure based on the finite element method. A critical plastic strain crack growth criterion is coupled with the numerical results to develop theoretical fracture toughness versus crack speed relationships for materials which separate in a locally ductile manner. For low rate sensitivity, the behavior is similar to that obtained earlier for rate-independent materials. On the other hand, for highly rate-sensitive materials, the toughness increases dramatically with speed for low speeds, but it levels off for higher crack speeds. The leveling off seems to be associated with the increasing apparent stiffness of the material associated with increasing crack tip speed.

Principal Investigator: L.B. Freund (Engineering).

Personnel: A.S. Douglas (Engineering).

Publications: "The Influence of Inertia on Elastic-Plastic Antiplane Shear Crack Growth", L.B. Freund and A.S. Douglas, Journal of the Mechanics and Physics of Solids, 30 (1982), 59-74.

"Dynamic Growth of an Antiplane Shear Crack in a Rate Sensitive Elastic-Plastic Material", L.B. Freund and A.S. Douglas, presented at the 2d ASTM International Symposium on Elastic-Plastic Fracture Mechanics, Philadelphia, 1981; to appear in Elastic-Plastic Fracture Mechanics.

Supported by the Materials Research Laboratory/NSF and NSF.

The Optical Method of Caustics in Plastic Fracture Mechanics

The shadow spot method, or the optical method of caustics, has been established as a valuable experimental procedure in fracture mechanics for measuring elastic stress intensity factors in planar fracture specimens. It has been observed, however, that if the crack tip deformation fields in specimens of ductile materials can be characterized by means of a single plastic intensity factor, analogous to the stress intensity factor in elastic fracture mechanics, then the shadow spot method has potential for use in measuring

this plastic intensity factor. The value of the J-integral has been adopted as the plastic strain intensity factor, and the lateral contraction of a planar specimen of power-law hardening material is calculated in terms of J on the basis of the so-called HRR asymptotic field of elastic-plastic fracture mechanics. For any given value of the hardening parameter n , the theoretical caustic curve which would be generated by geometrical reflection of normally incident parallel light from points of the deformed specimen surface lying well within the crack tip plastic zone is determined. It has been found that the value of J is proportional to the maximum transverse diameter of the shadow spot to the power $(3n + 2)/n$. The result provides a basis for direct measurement of fracture characterizing parameters in ductile metals and other ductile materials.

Principal Investigator: L.B. Freund (Engineering).

Personnel: A.J. Rosakis (Engineering), C.C. Ma (Engineering).

Publications: "Optical Measurement of the Plastic Strain Concentration at a Crack Tip in a Ductile Steel Plate", A.J. Rosakis and L.B. Freund, Journal of Engineering Materials and Technology, 104 (1982), 115-120.

"Caustic Curves Obtained by Numerically Simulating Reflection of Light Rays from the Surface Plane Stress Fracture Specimens", C.C. Ma, Sc.M. Thesis, Brown University (1982).

"Experimental Determination of the Fracture Initiation and Dynamic Crack Propagation Resistance of Structural Steels by the Optical Method of Caustics", A.J. Rosakis, Ph.D. Thesis, Brown University (1982).

Supported by the Materials Research Laboratory/NSF and the Office of Naval Research.

Fracture of Metals

In collaboration with Professor L.B. Freund, we are studying elastic-plastic fracture in structural metals. As part of this research we have developed two different experiments, the first intended for studies of fracture initiation and the second to study crack propagation in steels. The fracture initiation experiment employs a technique first

developed at Brown University. It is an adaptation of the split-Hopkinson bar in which a notched round bar with a fatigue precrack is loaded impulsively by a tensile wave propagating along the bar. The resulting loading wave provides a stress intensity rate, dK/dt , of about $10^6 \text{ MPa m}^{1/2} \text{ s}^{-1}$, i.e. a rate about ten times greater than that obtained in Charpy impact tests. However, the advantage of the present method over Charpy lies not in its high rate, but in the fact that this rate is combined with unambiguous records of average stress at the fracture site and of crack-opening displacement, both as functions of time. Hence the experimental results provide a dynamic value of K_{Ic} in the case of fractures that are primarily brittle and of J_{Ic} whenever the fracture is ductile. For crack propagation studies we employ wedge loaded double cantilever beam (DCB) specimens and we determine the values of K_{Id} directly by use of the optical method of caustics in reflection from the metal surface. We have constructed a Cranz-Schardin camera that provides a series of 12 different photographs of the caustic patterns as the crack advances in the DCB specimen. The exposure time of each photograph is approximately one microsecond and the time sequence of the 12 photographs can be selected arbitrarily between 7 and 700 microseconds after trigger. From the data provided in the photographs we are able to determine the values of K_{Id} at each position and thus find K_{Id} as a function of crack velocity. Our tests employing an AISI 4340 steel, for instance, show that K_{Id} is a monotonically increasing function of crack tip speed. It should be added that we have incorporated the effects of material inertia and of plastic deformation into our analysis of caustics, so that the expression we employ to evaluate the dynamic stress intensity factor is applicable to rapid crack propagation in structural metals.

In addition to the above, we have developed an analysis for the direct optical evaluation of the J integral characterizing the near tip field during fracture initiation in metals exhibiting a substantial amount of plastic flow in the vicinity of the crack tip. This method for determining the J integral has been verified by experiments on specimens heat-treated so their stress-strain behavior is very close to elastic-perfectly plastic.

As described in our previous report, in collaboration with Professor R. Asaro, we are continuing an investigation into the causes of fracture initiation in a typical structural steel, an AISI 1020 hot-rolled steel. The purpose of our experiments is to identify the micromechanisms, such as size and distribution of intergranular carbide platelets, prior austenite grain size, or size of pearlite colonies, leading to quasi-static and dynamic fracture. By employing the appropriate isothermal transformations, which we have now established for this steel, we are able to vary independently each of the different microconstituents

mentioned above. We are now preparing our first fracture specimens with these various heat treatments. After each test, sections through the fracture specimens will be examined microscopically to determine the location and origin of microcracks.

Principal Investigator: J. Duffy (Engineering).

Personnel: R.H. Hawley (Engineering), G.L. LaBonte, Jr. (Engineering), P. Rush (Engineering), H. Cocu (Engineering), A.J. Rosakis (Engineering), Y. Zuiki (Engineering), A. Azar (Engineering), E. Lavernia (Engineering), P. Rosakis (Engineering).

Publications: "Experimental Determination of the Fracture Initiation and Dynamic Crack Propagation Resistance of Structural Steels by the Optical Method of Caustics," A.J. Rosakis, Ph.D. Thesis, June 1982.

"Optical Measurement of the Plastic Strain Concentration at a Crack Tip in a Ductile Steel Plate," A.J. Rosakis and L.B. Freund, Journal of Engineering Materials and Technology, 104 (1982), 115-120.

"The Method of Caustics in the Presence of Crack Tip Plasticity," A.J. Rosakis and L.B. Freund, Proceedings 18th Annual Meeting of the Society of Engineering Science, Brown University, Providence, RI, (September 1981).

"The Effect of Tempering Temperature on Fracture Initiation in 4340 Steel," Y. Zuiki, M.S. Thesis, Brown University, Providence, RI, June 1982.

"The Effect of Thickness of a Double Canilever Beam on the Dynamic Stress Intensity Factor by the Optical Method of Caustics," A. Azar, Honors Thesis, Brown University, Providence, RI, June 1982.

Supported by the Materials Research Laboratory/NSF, Office of Naval Research, and the Army Research Office.

Correlation of Microstructure with Fracture Toughness

This program is concerned with correlating microstructure and fracture resistance in high strength steels, notably quenched and tempered 4340 steels. Microstructural

variables included prior austenite grain size and carbide size and distribution in the martensitic microstructures. A good correlation has emerged between the size distribution and spacing of carbides--in particular the larger undissolved particles--and the resulting fracture toughness. This correlation appears to explain observations reported in the literature of increasing fracture toughness coupled to decreasing ductility with increasing austenitizing temperatures. The higher austenitizing temperatures are more effective in treating the alloys and thus lead to more refined carbide sizes. To make the correlation, a model is used which combines estimates of the elastic-plastic fields ahead of cracks obtained from finite element calculations with micro models for fracture involving void initiation and coalescence by localized shear. The results of this study indicate the carbide size and spacing are important microstructural features that control toughness and also that distinct improvements in mechanical properties can be attained in high strength alloys through simple heat treatments. Future work will be directed at studies of more complex heat treatments that will hopefully combine the beneficial effects of high temperature heat treatments and effective solution treatment without the adverse effects of increased grain size, viz. decreased ductility.

Principal Investigator: Robert J. Asaro (Engineering).

Personnel: L. Hermann (Engineering) and S. Lee (Engineering).

Supported by the United States Department of Energy (DOE).

Oxidation and Fracture Characteristics of Reaction Bonded Silicon Nitride (RBSN)

The application of high strength ceramic materials for high temperature components in gas turbine engines not only requires that these normally brittle materials exhibit high strength, toughness, and creep resistance at elevated operating temperatures, but also that they stand up to the hot corrosive and erosive atmospheres within the turbine engines. This requires that any oxidation of RBSN not result in the formation of surface flaws, oxide penetration of grain boundaries or internal oxidation of unreacted silicon within the volume of the material. It also requires that any surface flaws in the RBSN be sealed by the surface treatment to prevent these flaws from acting as fracture initiation sites in service.

A coating technique has been developed to provide high temperature oxidation resistance and hot corrosion resistance to RBSN components. Thick coatings of reactively sputtered silicon nitride were deposited onto reaction bonded silicon nitride surfaces to form an effective oxygen diffusion barrier by eliminating all short circuit paths to the interior and to seal off all surface flaws. To accomplish this, amorphous films of silicon nitride were deposited and then heat treated to effect crystallization of the coating. The as-deposited amorphous and subsequently crystallized films have been characterized and, by means of this coating technique, the oxidation of the underlying RBSN can be substantially reduced in the temperature range 1000-1200°C by the deposition and crystallization of a 5 μm thick coating of silicon nitride.

Principal Investigator: Marc H. Richman (Engineering).

Personnel: O.J. Gregory (Engineering) and J.W. Fogarty (Engineering).

Publications: "Reactive Sputter Coated Reaction Bonded Silicon Nitride," O.J. Gregory and M.H. Richman, Thin Solid Films, 91 (1982) 163.

"Nitridation of High Purity Single Crystal Silicon," O.J. Gregory and M.H. Richman, Metallography, 15 (1982) 157.

"Strength and Fracture Toughness of Reaction Bonded Si_3N_4 ", S.C. Danforth and M.H. Richman, to be published in the Bulletin of the American Ceramics Society.

Supported by the Materials Research Laboratory/NSF.

Plastic Shear Localization from Inhomogeneous States

Work in this area is continuing with particular emphasis on localization phenomena at a blunting crack tip. Our previous work (Needleman and Tvergaard, to be published in an ASTM STP) has given an initial picture of shear band development at a crack tip in a solid characterized by a plastic flow rule with a vertex on the yield surface. The current series of finite element studies are being carried out in conjunction with experimental studies on bend specimens with machined notches. The radii of curvature of the notches is varied to encompass situations where the highly deformed notch tip region spans from a few grains to many grains. The materials being used in the experiments include high and ultra high strength steels. The analyses

are based on a vertex theory of plasticity. By using such a theory the presumption is that stability against flow localization is limited by the plastic flow process itself. A major aim of this study is to provide a precise comparison between theory and observation on localized shearing and its role in fracture initiation at a crack tip.

Principal Investigators: Robert J. Asaro (Engineering) and Alan Needleman (Engineering).

Personnel: V. Freudmann (Engineering).

Publications: "On the Development of Shear Bands in Pure Bending", N. Triantafyllidis, A. Needleman and V. Tvergaard, Int. J. Solids Struct., 18 (1982) 121-138.

"Instability and Failure of Internally Pressurized Ductile Metal Cylinders," M. Larson, A. Needleman, V. Tvergaard and B. Storakers, J. Mech. Phys. Solids, 30 (1982) 121-154.

"Crack Tip Stress and Deformation Fields in a Solid with a Vertex on its Yield Surface", A. Needleman and V. Tvergaard, ASTM STP, in press.

"On the Finite Element Analysis of Localized Plastic Deformation", A. Needleman and V. Tvergaard, to be published.

Supported by the Department of Energy, and NSF/Solid Mechanics.

Single Crystal Plasticity

The constitutive equations developed previously (Peirce, Asaro and Needleman, Acta. Met., 1982, p. 1087) for the elastic-plastic deformation of single crystals have generalized to account for material rate sensitivity. One important reason for accounting for material rate dependence is the inadequacy of a rate independent theory for the pronounced latent hardening frequently observed experimentally. In our previous (rate independent) numerical studies of nonuniform deformation in single crystals oriented for double slip a "patchy" pattern of slip developed when the latent hardening rates were sufficiently larger than the self hardening rates; that is, the gage section broke up into a slip mode characterized by

contiguous regions, "patches", in which slip was concentrated on one slip system or the conjugate system or on both. The full implications of this "patchy" slip could not be explored within the context of the rate independent theory, since the numerical procedure broke down for latent hardening rates above a critical value (which could be determined by a rate independent bifurcation analysis). Our rate dependent model does permit analyses of "patchy" slip to be carried out for a full range of latent hardening ratios. Associated with this phenomenon of patchy slip are fundamental questions of uniqueness of the choice of active slip systems and in predicted lattice rotations. The kinematics of the lattice becomes indeterminate when the slip mode is not unique because the relative rotation of the lattice with respect to macroscopic material directions depends on the choice of active systems. This in turn has implications of fundamental importance for describing polycrystalline constitutive response at finite strains and, in particular, for the development of texture. Numerical studies of the development of "patchy" slip in rate sensitive single crystals and the implications for polycrystalline behavior are currently being explored.

Principal Investigators: Robert Asaro (Engineering) and Alan Needleman (Engineering).

Personnel: Daniel Peirce (Engineering).

Publication: "An Analysis of Nonuniform and Localized Deformation in Ductile Single Crystals", D. Peirce, R.J. Asaro and A. Needleman, Acta. Met., 30, Overview 21 (1982), 1087-1119.

Supported by the Materials Research Laboratory/NSF and NSF (Metallurgy Section).

Viscoplastic Analysis of Cracks Under Static and Dynamic Conditions

Time dependent deformation has been observed at room temperature and higher temperatures in several structural steels (e.g., A533B and 304 stainless steels). The deformation of these loading rate dependent materials is modelled by a viscoplastic constitutive relation. Crack tip fields were computed for loading rates that varied over six orders of magnitude. These results coupled with fracture criterion based on a critical stress or critical strain suggest that under certain conditions, the value of K at crack initiation is loading-rate dependent. Furthermore,

strain controlled crack growth could be initiated at some point during sustained loading.

Principal Investigator: C.F. Shih (Engineering).

Publications: "On the Time and Loading Rate Dependence of Crack-tip Fields at Room Temperature - Viscoplastic Analysis of Tensile Small-Scale Yielding," M.M. Little, E. Krempl and C.F. Shih, accepted for publication in ASTM-STP.

"Viscoplastic Analysis of a Compact Tension Specimen in Mode I Loading," M. M. Little, E. Krempl and C.F. Shih, manuscript under preparation.

Supported by the Materials Research Laboratory/NSF.

SECTION 3

Inorganic Glasses

Introduction

The Inorganic Glasses Group focuses its research on understanding the structures, relaxation phenomena, and electronic states and properties of the three main types of inorganic glasses: ionic and non-ionic oxide glasses; amorphous semiconductors; and amorphous metals. Fundamental issues concerning the amorphous state are being addressed by studying each of these types of materials and by developing new theoretical and experimental methods for their investigation.

Among the significant advances achieved in this year and reported briefly in this section are the following. First, in studying the picosecond decay of photoinduced changes of the absorption coefficient in α -Si:H doped with P, Tauc found that instead of the induced absorption observed in his previous work the induced absorption changed very fast into induced transmission. This has been interpreted as being due to carriers which get trapped in low energy states where their absorption cross-section is very small. Through this work Tauc could follow the motion of carriers into deep traps starting at times less than 5 ps, and showed that the transport is dispersive starting at extremely short times. Second, Risen has devised a method based on the mixed alkali effect for elucidating important aspects of strain and its thermal treatment in glasses. He has shown that the production of intrinsically strained units, which result from cation size mismatches, exhibit the same type of spectroscopic phenomena manifested by unannealed single alkali glasses, and has separated these effects through thermal treatment. This constitutes a systematic approach to understanding the production and relief of strain in glasses and the molecular structures and events involved. Third, Elbaum has shown that two stages exist in the amplitude-dependence of ultrasonic attenuation in metallic glasses; the first, at relatively low amplitudes, has the features predicted by the TLS tunneling theory, but the second, with a much higher amplitude dependence, does not. Fourth, Kosterlitz has succeeded in recasting the long-range model for spin glasses into a more tractable form in which the following results were obtained: the susceptibility and entropy are properly treated, and the Edwards-Anderson order parameter found is inconsistent with the Toulouse-Parisi projection hypothesis. Fifth, Bray has obtained a number of

experimental results which elucidate the dependences of structure and bonding on preparative history of glasses, including showing that the fraction of four-coordinated B in zinc borates depends on thermal history, that significant amounts of BeO are present in NaF-BeF₂ glasses as typically prepared, and that a new structural model is required for sodium borosilicate glasses at high soda content. Finally, several new results on ion motion in inorganic glasses are reported, including Cole's development of highly accurate TDS methods, Cole and Risen's approach to TDS measurements on mixed alkali glasses, and Bray's findings by ¹⁹F-NMR that some F-ions are mobile at room temperature in ZrF₄-BaF₂-LaF₃ glasses and at 130°C in NaF-BeF₂ glasses.

The following reports indicate some completed work. Other projects on inorganic glasses, including fast ionic conductors, are underway.

SECTION 3

Inorganic Glasses

Individual Contributions

Time Resolved Spectroscopy of Amorphous Semiconductors

We continued our studies of the decays of photoinduced absorption in amorphous silicon (a-Si) and amorphous hydrogenated silicon (a-Si:H) in the time domains of 0.5 to 200 psec and 500 nsec to 10 msec as a method for studying the carrier dynamics and electron states in these materials.

We showed that the decay of the infrared photoinduced absorption band in a-Si:H can be used for determining the dispersion parameter. In a joint project with the Harvard group of Prof. Paul we compared our results with the data obtained at Harvard by the time-of-flight experiment which is the standard method for measuring the dispersion parameter. We found very good agreement which has strengthened the interpretation of the photoinduced absorption in a-Si:H proposed by us as due to optical reexcitation of trapped holes whose concentration decreases by recombination with more mobile electrons.

We showed how the measurement of the photoinduced absorption in a-Si:H can be used for determining the energy distribution of states in the tails close to the band edges.

Our most spectacular results were obtained by studying the picosecond decay of photoinduced changes of the absorption coefficient in a-Si:H doped with phosphorus. Instead of induced absorption observed in all our previous work we observed a very fast change of induced absorption into induced transmission. This was interpreted as due to carriers which get trapped in low energy states where their absorption cross-section is very small. An important result of this work is that we could follow the motion of carriers into the deep traps starting at times shorter than 5 psec and determine the parameters of this motion. We convincingly showed that the transport is dispersive starting at such extremely short times, and can be described by the multiple trapping model.

Principal Investigator: Jan Tauc (Engineering and Physics).

Personnel: Z. Vardeny (Engineering), S. Ray (Physics), J. Strait (Physics), D. Pfof (Physics).

Publications: "Comparison of the dispersion parameters from

time-of-flight and photo-induced midgap absorption measurements on sputtered a-Si:H", P.B. Kirby, W. Paul S. Ray and J. Tauc, Sol. State Communications, 42 (1982), 533.

"Studies of the band tails in a-Si:H by photomodulation spectroscopy", J. Tauc, Solar Energy Materials, 8 (1982), 259.

"Picosecond photoinduced transmission associated with deep traps in phosphorous doped a-Si:H", Z. Vardeny, J. Strait, D. Pfost, J. Tauc and B. Abeles, Phys. Rev. Lett., 48 (1982), 1132.

"Photoinduced absorption in amorphous silicon", J. Tauc, Festkörperprobleme XXII (Vieweg, Braunschweig), (1982), 85.

"Optical picosecond studies of carrier dynamics in amorphous semiconductors", Z. Vardeny, Proc. Laser 81 Conference, STS Press, McLean, VA (1982), 892.

"Ultrafast relaxations of photoinduced carriers in amorphous semiconductors", Z. Vardeny, J. Strait and J. Tauc, Picosecond Phenomena III, K.B. Eisenthal, R.M. Jochstrasser, W. Kaiser and A. Lauberau (eds.), Springer Verlag.

"Ultrafast relaxations of photogenerated carriers in amorphous semiconductors", J. Tauc, to appear in Proceedings of the 16th International Conference on the Physics of Semiconductors, Montpellier (1982).

"Picosecond electronic relaxations in amorphous semiconductors", Z. Vardeny and J. Tauc, review paper to appear in Semiconductor Processes Probed by Ultrafast Laser Spectroscopy, R.R. Alfano (ed.), New York: Academic Press.

Supported by the Materials Research Laboratory/NSF and NSF.

Spin Glasses

The study of the long-range⁽¹⁾ model for spin glasses was continued. A solution of this model near the spin glass temperature was obtained by Parisi⁽²⁾ near the critical temperature but no analytic solution has been obtained near zero temperature. Although differential equations from which the partition function may in principle be calculated were previously written down.

We succeeded in recasting the equations into a more

trackable form and obtained the following results:

- a) the susceptibility $X = 1$ for all $T \leq T_c$
- b) the entropy $S = 0$ at $T = 0$
- c) the Edwards-Anderson order parameter --
 $q(T) \approx 1 - 1.53T^2$ for $T \approx 0$

The first result, although obtained numerically by Parisi⁽²⁾ has not been proved before and this is the first demonstration of the second result. Although this is obviously true for an Ising system, all previous approaches have given a negative zero temperature entropy. The last result is inconsistent with the Toulouse-Parisi projection hypothesis⁽³⁾. A paper on this is in preparation.

(1) D. Sherrington and S. Kirkpatrick, Phys. Rev. Lett., 35, 1972 (1975).

(2) G. Parisi, Phys. Rep., 67, 25 (1980).

(3) G. Parisi and G. Toulouse, J. Physique Lett., 41, L361 (1980).

Principal Investigator: J.M. Kosterlitz (Physics).

Supported by the Materials Research Laboratory.

Ultrasonic Studies of Metallic Glasses

We have previously reported a series of ultrasonic observations on two families of metallic glasses (PdSiCu, PdNiSi) at low temperatures (below ~1K). The results showed that in these materials ultrasonic attenuation as a function of amplitude, frequency and temperature does not behave in accordance with predictions of the two-level system (TLS) tunneling theory. We have since then found that two stages exist in the amplitude dependence of ultrasonic attenuation in metallic glasses at low temperatures. One of these stages (the "first") occurs at relatively low amplitudes and has the frequency and temperature dependence predicted by the TLS tunneling theory. At higher amplitudes this is followed by the stage which we previously observed. This ("second") stage is the one we previously observed and discussed; it is characterized by an amplitude dependence which can be several powers of ten larger than the "first" stage and has the frequency and temperature dependence

described earlier.

Principal Investigator: C. Elbaum (Physics).

Personnel: A. Hikata (Applied Mathematics) and G. Cibuzar (Physics).

Publications: "Ultrasonic Attenuation in Metallic Glasses at Low Temperatures", G. Park, A. Hikata and C. Elbaum, Journal de Physique, 42 (1981), C5-517.

"Ultrasonic Studies of Metallic Glasses at Low Temperatures, G. Park, A. Hikata, and C. Elbaum, Phys. Rev. B24 (1981), 7389.

"Existence of Two Stages in Amplitude-Dependent Attenuation of Ultrasonic Waves in Metallic Glasses", A. Hikata, G. Cibuzar and C. Elbaum, J. Low Temp. Phys., 49 (1982), 339.

Supported by the Materials Research Laboratory and NSF.

Intrinsic Strain in Mixed Alkali Glasses

The ability to control the composition variable in ionic oxide glasses to elucidate structural features and to systematize the variations in physical properties of glasses is exercised in construction series of mixed alkali glasses, such as $x\text{Cs}_2\text{O}(1-x)\text{Na}_2\text{O}\cdot 5\text{SiO}_2$. Through Brillouin and far infrared studies of this system and a theoretical approach to understanding mixed alkali effects on its members' transport properties, we have developed a model for interpreting mixed alkali effects on dynamic mechanical properties. The key aspect of the model is the production of strained units which result from cation size mismatches, cause the introduction of new relaxation mechanisms, and are accompanied by the sort of broad distribution of network bond angles that characterize the more highly disordered forms glasses have before annealing. To identify such units and to employ the alkali mixing to force annealed glasses to manifest a specific form of behavior exhibited before annealing, the Raman spectra of this series of glasses have been obtained as a function of both x and annealing conditions. It was found, indeed, that the spectral manifestations of alkali mixing in annealed systems are the same as those shown by unannealed single alkali glasses that are reduced or eliminated by annealing. These results are

being analyzed in terms of both the annealing process and the mixed alkali effects on dynamic mechanical properties.

Principal Investigator: William M. Risen, Jr. (Chemistry).

Personnel: E.I. Kamitsos (Chemistry).

Publication: "Spectroscopic Studies of Mixed Alkali Pentasilicate Glasses", E.I. Kamitsos and W.M. Risen, Jr., J. Noncryst. Solids, in press (1982).

Supported by the Materials Research Laboratory/NSF and ONR.

B¹¹ NMR Studies and Structural Modeling of Na₂O-B₂O₃-SiO₂ Glasses of High Soda Content

NMR techniques have been employed to determine the relative fractions of boron atoms in various bonding arrangements in Na₂O-B₂O₃-SiO₂ glasses of high soda content. The data show that if enough Na₂O is added, four-coordinated borons are destroyed and borons with one or two non-bridging oxygens are created, but that both the beginning point and the rate of these processes depend strongly on the amount of silica present. These findings are quantitatively inconsistent with structural models previously suggested in the literature. Utilizing the concept of proportionate atomic sharing of the additional Na₂O, a new structural model has been proposed for $K \leq 8$ ($K = \text{mol\%SiO}_2 / \text{mol\%B}_2\text{O}_3$) which is consistent with all the data, including previously reported data for glasses in the region of relatively low soda content. Using $R = \text{mol\%Na}_2\text{O} / \text{mol\%B}_2\text{O}_3$, the new model states that for

$$R_{\text{MAX}} = 1/2 + 1/16K \leq R \leq R_{\text{D1}} = 1/2 + 1/4K,$$

all the additional Na₂O is employed in forming non-bridging oxygens on the silica tetrahedra; then, for $R_{\text{D1}} \leq R \leq R_{\text{D3}} = 2+K$, the fraction $(K+K/4)/(2+K)$ of the additional Na₂O destroys reedmegnerite groups and forms pyroborate units plus silica tetrahedra with two non-bridging oxygens per Si atom, while the fraction $(2-K/4)/(2+K)$ of the additional Na₂O destroys diborate groups and forms additional pyroborate units.

Principal Investigator: P.J. Bray (Physics).

Personnel: Warren J. Dell (Physics).

Supported by the Materials Research Laboratory.

Dependence of Structure and Bonding on Temperature

Recent reports have attributed the change in boron coordination in CuO-doped sodium borate glasses prepared in alumina crucibles at different temperatures to the effect of differences in thermal agitation at various temperatures. By preparing glasses of the same composition with platinum crucibles and alumina crucibles at different temperatures and comparing their B^{11} and Al^{27} NMR response, it has been shown that the change is due to temperature-dependent aluminum contamination from the crucibles. Studies on the zinc borate system have found that, for glasses within a composition region around 60 mol% ZnO, glasses cooled slowly have a higher fraction of four-coordinated borons (N_4) than glasses cooled rapidly. N_4 measurements, taken at 500K, on a series of sodium borosilicate glasses and a series of sodium alumino-borosilicate glasses are in progress. These are to be compared with room temperature measurements to determine whether N_4 is reduced at the higher temperature as predicted by Dr. Roger Araujo of Corning Glass. A twin-roller quenching device with a temperature-controlled furnace is under construction for use in obtaining high quench rates from selected melt temperatures.

Principal Investigator: P.J. Bray (Physics).

Personnel: M.L. Lui (Physics).

Supported by NSF and the Owens-Corning Fiberglass Corporation.

7Li NMR in Superionic Conducting Glasses

7Li NMR investigations of superionic conducting glasses in the $Li_2O-Li_2Cl_2-B_2O_3$ system indicate the presence of two distinct species of Li in glasses of high Li content (~50

mol%). These species have been identified with 1) stationary and 2) highly mobile Li ions. The relative populations of the two species have been found to vary with temperature. Measurements performed at temperatures up to the glass transition temperature, indicate that the stationary ions are thermally activated to become mobile with an activation energy of about 0.16 eV. Once mobile, only very small amounts of thermal energy are necessary to increase significantly the rate of motion.

Principal Investigator: P.J. Bray (Physics).

Personnel: David Hintenlang (Physics).

Supported by the Materials Research Laboratory.

NMR of Fluoro-Zirconate Glasses

Fluorine NMR investigations of glasses in the system $\text{ZrF}_4\text{-BaF}_2\text{-LaF}_3$ have revealed the presence of two distinct fluorine sites. The NMR spectrum exhibits a narrow temperature dependent line superimposed on a broader line. This narrow line is present even at temperatures as low as 25°C, indicating that some halide ions are mobile in these glasses at room temperature. Details of the motion are under investigation via measurements of the spin-lattice (T_1), spin-spin (T_2), and rotating frame spin-lattice ($T_{1\rho}$) relaxation times as a function of temperature and glass composition.

Principal Investigator: P.J. Bray (Physics).

Personnel: Robert Mulkern (Physics).

Supported by Xerox Corporation.

B^{11} and Pb^{207} NMR Studies of Glasses in the System $xFe_2O_3-yPbO-zB_2O_3$ ($0 \leq x \leq 15.3$ mol%, $z/y=3$)

Ten glasses in the system $xFe_2O_3-yPbO-zB_2O_3$ ($0 \leq x \leq 15.3$ mol%, $z/y=3$) were fabricated and characterized using chemical analysis and x-ray, density, and magnetic susceptibility measurements. The following room temperature NMR measurements were performed: 1) the peak to peak width of the 4-coordinated B^{11} response was measured as a function of Fe_2O_3 content and applied field; 2) the B^{11} NMR spectrum due to 3-coordinated borons was obtained for each sample; 3) N_4 , the fraction of 4-coordinated borons, was determined using the area method; and 4) the Pb^{207} NMR spectrum was obtained for each sample. The linewidth data were interpreted in terms of a Voigt broadening lineshape which contains both field-dependent and field-independent components. B^{11} NMR lineshape, N_4 , and Pb^{207} NMR data were analyzed in terms of changes in the borate structural network. Two-region behavior is exhibited by the N_4 , Pb^{207} NMR absorption peak position, and density data. A computer simulation study of the effects of Gaussian and Lorentzian broadening on the determination of N_4 using the area method was performed and indicates that the presence of Lorentzian broadening in the NMR lineshape can adversely affect the N_4 measurement.

Principal Investigator: P.J. Bray (Physics).

Personnel: Frank Bucholtz (Physics).

Supported by the Materials Research Laboratory/NSF.

Be^9 and F^{19} NMR in BeF_2 -based glasses

Glasses in the $NaF-BeF_2$ system have been studied by Be^9 and F^{19} NMR. Nominally pure BeF_2 produces an NMR response that indicates the presence of two distinct Be sites. After extensive experimentation it was concluded that the narrow response is due to about 7% BeO impurities. This is a very important finding since such impurities would be expected to have a drastic effect on the transparency of these materials. The binary glass does not exhibit this effect, suggesting that the alkali ion "purifies" the network by forcing the oxygen into other bonding arrangements. The large Be^9 quadrupole coupling constant observed in $NaF-BeF_2$ glasses provides strong evidence for the presence of five

coordinated Be in these materials. F^{19} NMR shows the emergence of a narrow response at about 130°C in the binary samples, suggesting that some F^{19} ions become mobile in this temperature range.

Principal Investigator: P.J. Bray (Physics).

Personnel: W. Dell (Physics).

Supported by NSF.

Si^{29} Studies of Alkali Silicate Glasses

Continuous wave NMR studies of naturally abundant Si^{29} in potassium silicate glasses and polycrystalline compounds have shown that structural information can be obtained from the anisotropic chemical shift at frequencies as low as 10 MHz. The small magnetic moment of the potassium nucleus yields relatively small dipolar broadenings in these glasses and compounds. But the broadening still interferes with extraction of structural information from the NMR spectra. A program of study of these materials at higher frequency (49.6 MHz) has begun with the utilization of a Bruker WM-250 pulsed spectrometer in the Brown Chemistry Department. Because the chemical shift increases with frequency while the dipolar broadening is frequency independent, resolution can be improved by about a factor of 5. The studies will include lithium and sodium silicates.

Principal Investigator: P.J. Bray (Physics).

Personnel: S. J. Gravina (Physics).

Supported by NSF.

O^{17} NMR of SiO_2

An O^{17} -enriched amorphous SiO_2 sample had been heat-treated to produce α -cristobalite whose production was confirmed by x-ray studies. The heat treatment was continued until the

amorphous background in the x-ray powder pattern had been reduced to a flat baseline. The long spin-lattice relaxation time (T_1) in α -cristobalite causes saturation effects, and the usual derivative absorption mode spectrum will only be obtained after reduction of T_1 . However, on comparing the 0^{17} high-power dispersion mode spectrum of α -cristobalite with that of amorphous SiO_2 , it was found that the latter has broader features, reflecting the effect of a distribution of quadrupole parameters arising from a distribution of bond angles. Arrangements are now being made for the irradiation of the α -cristobalite sample to reduce T_1 so that the absorption mode spectrum may be obtained. Quantitative values for the quadrupole parameters will then be obtained by computer simulation of the lineshape.

Principal Investigator: P.J. Bray (Physics).

Personnel: M. Lui (Physics).

Supported by NSF and Owens-Corning Fiberglass Corporation.

Low Frequency NQR of B^{10} and B^{11}

It has been found in this laboratory that B^{10} and B^{11} NQR signals cannot be detected by pulsed spin echo techniques with current pulsed spectrometers. To study these nuclei, a continuous-wave Robinson-type spectrometer has been designed and is being built. The entire oscillator part of the spectrometer is designed to operate at 77K using low noise MOSFETS. Crystalline B_2O_3 and other borate polycrystalline powders will be studied. Comparison of NQR results with existing NMR data of borate glasses will add to an understanding of how closely the short-range order in a glass matches that of the crystalline compounds of the glass-forming system. This spectrometer will also be a valuable probe for other low-frequency NQR and NMR studies, since current NMR spectrometers have poor sensitivity at frequencies below 2 MHz.

Principal Investigator: P.J. Bray (Physics).

Personnel: Samuel J. Gravina (Physics).

Supported by NSF.

Time Domain Spectroscopy of Glasses and Conducting Dielectrics

The principal research effort by the principal investigator has been development of two new experimental methods for high frequency dielectric measurements in the frequency range 500KHz to 5GHz or higher. Both use repetitive sampling methods to obtain time resolved digitally averaged records of voltage unbalance in two channels of coaxial line bridge network, one terminated by the unknown of interest and the other by a suitable reference standard. Either pulse excitations with 50 picosecond response time or sine wave excitations, from 500 KHz to 250 MHz at present, can be used.

A general analysis of the methods assuming only linear response behavior makes it possible to calibrate and correct for effects of impedance mismatch and system responses by comparison of known standards. This, together with bridge conformations for differential measurements, makes possible measurements of high precision over wide frequency or time ranges with the same basic equipment.

An extensive series of tests and calibrations have demonstrated the validity of the methods. These were delayed considerably by breakdowns of both sampling and signal averaging equipment, both finally corrected. When complete, measurements should soon be possible on a series of mixed alkali oxide-silicate glass prepared by W.M. Risen and co-workers and studied by using IR and Raman spectroscopy.

The basic facility has been used by two visiting scientists in the past year. A. H. Fawcett (Queens University, Belfast) has studied dielectric properties of a series of poly (olefin sulfone) copolymers in solution to obtain information about kinetics of side chain motions. G. Deblos (CNRS, University of Bordeaux) has studied microemulsion systems (water/toluene/sodium dodecyl sulfate-n-butyl alcohol cosurfactant) over wide composition ranges and discovered relaxations near 1GHz attributed to mobile hydroxyl groups of water and alcohol of the surface layers of microdroplets or channels. Paul Winsor IV assisted greatly with both projects, as well as continuing measurements of electrolyte solutions.

Principal Investigator: R.H. Cole (Chemistry).

Personnel: Paul Winsor IV (Engineering).

Publications: "Dielectric Properties of Electrolyte Solutions: 1. Sodium Iodide in Seven Solvents at Various Temperatures", P. Winsor IV and R.H. Cole, J. Phys. Chem. 86 (1982) 2486.

"Dielectric Properties of Electrolyte Solutions: 2. Alkali Halides in Methanol", P. Winsor IV and R.H. Cole, J. Phys. Chem. 86 (1982) 2491.

Supported by NSF (Winsor), University Grants Committee, Britain (Fawcett), CNRS, France (Delbos).

SECTION 4

Solid Surfaces

Introduction

A central theme of the research program in solid surfaces is the development of microscopic models of static properties, such as the atomic geometry and the electronic structure, which in turn can serve as the basis for an understanding of dynamic processes, such as scattering, adsorption, and surface chemical reactions. For this purpose a range of model systems are studied, by a number of experimental and theoretical techniques.

In the period covered by this report most of the structural studies have been focused on surface phase transitions, and on their physical and chemical consequences. Estrup and Stiles have done experiments on several tungsten and molybdenum surfaces to establish their phase diagrams in the temperature-coverage plane. At the same time, these systems have been studied theoretically by Roelofs and Ying using several model Hamiltonians, as well as Monte Carlo techniques.

Studies of dissociation and desorption for various adsorbate-substrate combinations, reported by Estrup and by Greene, show a clear dependence of the kinetics on structural phase transitions, a topic which deserves additional detailed investigations. In other kinetic studies, Risen has used transition metal clusters in ionomers to successfully model surface chemical reactions.

In a newly started project, Diebold has used a laser technique--resonantly enhanced multiphoton ionization--to measure the energy exchange of molecular NO with a metal surface. Greene, in another scattering experiment, has measured the rate and efficiency of ionization of a series of alkali atoms incident on well-defined solid surfaces.

SECTION 4

Solid Surfaces

Individual Contributions

Inelastic Scattering of Diatomic Molecules from Solid Surfaces

Resonantly enhanced multiphoton ionization was used to determine rotational state distributions of NO scattered from a Cu surface in a high vacuum. A pulsed valve produced a high intensity beam of NO seeded in He with a well-defined translational energy and a rotational temperature of 7K. The beam from a nitrogen laser pumped dye laser was focused into the scattering region. NO was pumped via the C state in a three-photon nonlinear absorption process to give NO⁺ which was detected by a channel electron multiplier. By scanning the laser over the C-X band system a spectrum was obtained, which, with a theoretical calculation of two-photon linestrengths, permitted determination of rotational and spin-orbit population distributions. The most important conclusions from this study are that for the rotational states detected, a Boltzman population distribution is found and that the nature of the NO-surface collision is primarily impulsive at the energies studied. The temperature dependence of the rotational accommodation coefficients found here is in agreement with the predictions of the hard cube model.

Principal Investigator: G.J. Diebold (Chemistry).

Personnel: J.S. Hayden (Chemistry).

Publication: "Multiphoton Ionization Detection of NO Scattered from Solid Surfaces," J.S. Hayden and G.J. Diebold, J. Chem. Phys. (in press).

Supported by the Materials Research Laboratory/NSF.

Commensurate-Incommensurate Transition for H/W(100)

In H/W(100), beyond a coverage of approximately 0.3 monolayers, the commensurate $c(2 \times 2)$ ordered phase goes over into an incommensurate one. The occurrence of this transition is somewhat puzzling because of the short range nature of interactions both between H atoms and W atoms. We have found that there is a strong component of indirect H-H interaction mediated by the soft mode of the W-surface. This could possibly account for the occurrence of the incommensurate phase. Another way of understanding this transition is to integrate out the H degrees of freedom to obtain an effective lattice dynamic Hamiltonian. We have successfully performed this calculation and are now analyzing the soft mode of this effective Hamiltonian as a function of coverage and temperature.

Principal Investigator: S.C. Ying (Physics).

Personnel: L. D. Roelofs (MRL) and G.Y. Hu (Physics).

Supported by the Materials Research Laboratory/NSF.

Structural Phase Transition in Quasi-two Dimensional Systems

The structural phase transition observed on solid surfaces with and without chemisorbed species have been found to be the realization of many two-dimensional model Hamiltonians. For example, the Ising model and the X-Y model with cubic anisotropy are appropriate for H/W(100) under different experimental conditions. We have been studying these Hamiltonians by a combination of real space renormalization group and Monte Carlo simulation techniques. The detailed behavior of both the long range order and short range order are determined in different regions of the phase space.

Principal Investigator: S.C. Ying (Physics).

Personnel: L.D. Roelofs (MRL) and G.Y. Hu (Physics).

Publications: "Structural Phase Transition on W and Mo

Surfaces", S.C. Ying and L.D. Roelofs, invited Paper at the second Trieste International Symposium on Statistical Mechanics of Adsorption (1982).

"Compatibility of FIM and LEED observations for the W(001) Reconstruction," P.J. Estrup, L.D. Roelofs and S.C. Ying, to appear in Surface Science.

Supported by the Materials Research Laboratory/NSF.

Phase Diagrams For Models of Surface Phase Transitions

Some systems exhibiting surface reconstruction, such as H/W(100), can be modeled using Hamiltonians based on continuous dynamical variables. (In the case of H/W(100) the variables are the W atom displacements from bulk-like positions.) We have worked on methods for calculating phase diagrams of such models, for the purpose of comparison with experiments on systems on which the models are based.

We have developed a Migdal renormalization group (RG) scheme which seems to give highly accurate phase diagrams for models of this type. We have done extensive calculations on the ϕ^4 model and the planar model in two dimensions. The former may be useful in describing some reconstructions with vertical displacements while the latter, we have shown, can be applied to the H/W(100) system after integrating out the H degrees of freedom, using a mean field approximation.

To check the RG results, we have also developed with the assistance of G.-Y. Hu, a Monte Carlo simulation program for both models. This also allows detailed checking of correlation functions away from transition temperatures to answer questions of experimental and theoretical interest.

Principal Investigator: L.D. Roelofs (MRL).

Personnel: G.-Y. Hu (Physics).

Publications: Proc. 2nd International Conference on the Statistical Mechanics of Adsorption, Trieste, Italy (1982), L.D. Roelofs and P.J. Estrup, to be published in Surf. Sci.

Proc. 2nd International Conference on the Statistical Mechanics of Adsorption, Trieste, Italy (1982), S.Y. Ying and L.D. Roelofs, to be published in Surf. Sci.

L.D. Roelofs, G.-Y. Hu and S.C. Ying (in preparation).

Supported by the Materials Research Laboratory/NSF.

The Scattering and Ionization of Atoms at Surfaces

The rate and efficiency of ionization of Cs, K, Na, and Li atoms incident on Si(111) and Si(100) surfaces vary with the state of the surface as well as its temperature; they reveal phase transitions occurring on the surfaces at ca 1100 and 950K respectively. The measurements give values for the work function, and the energies of adsorption of the atoms as well as information about their mobility on the surface. Other experiments now being done on SiC and graphite show related but appreciably different behavior that will help to characterize these surfaces also.

An apparatus for the study of the angular and energy distributions of atoms scattered from crystals has produced diffraction peaks for a beam of He scattered from LiF and will be used next for beams of He and Ar on the (0001) plane of graphite.

Principal Investigator: E.F. Greene (Chemistry).

Personnel: A. LeGrand (Physics), J. Keeley (Chemistry), and M. Pickering (Chemistry).

Publication: "Interaction of K, Na, Li, and Tl with Silicon (111) and (100) Surfaces; Surface Ionization and Kinetics of Desorption", E.F. Greene, J.T. Keeley and M.A. Pickering, Surface Science, 120 (1982), 103-126.

Supported by the Materials Research Laboratory/NSF and the U.S. Department of Energy.

Experimental Studies of Chemisorption

The kinetics of dissociation and desorption of chemisorbed molecules have been investigated. Isothermal rate data are obtained by means of a method previously developed in this laboratory whereby the instantaneous coverage of a given

species is monitored by photoelectron spectroscopy and Auger spectroscopy. Data for CO/Mo(100) and CO/Mo(110) indicate that the dissociation energy is strongly dependent on coverage and a study of the origin of this unexpected effect is underway.

Optical studies of single-crystal metal surfaces have been continued. The extension of SRS (surface reflectance spectroscopy) to near IR is being explored, and the feasibility of combining SRS with electric field modulation is under study. In collaboration with G. J. Diebold, a new project has been started which attempts to apply laser-induced multi-photon ionization spectroscopy to chemisorbed molecules.

Principal Investigator: P.J. Estrup (Physics and Chemistry).

Personnel: J. Erickson (Chemistry) and J. Prybyla (Chemistry).

Supported by the Materials Research Laboratory/NSF.

Surface Reconstruction of bcc Transition Metals

Experimental studies have been carried out concerning the reconstruction of single-crystal surfaces of tungsten and molybdenum. The phase diagram for the H/W(001) chemisorption system has been extended to higher coverage and temperature, and it has been found that the W atom displacements persist up to the desorption temperature. The results indicate that the reconstruction exerts a dominating influence on the desorption kinetics. In order to obtain more detailed structural data for the phase transitions on these surfaces, equipment for rapid LEED data acquisition has been assembled. It permits simultaneous measurement of the intensity of many beams in a LEED pattern as a function of time (coverage, temperature). In addition, the angular profile of the beam can be obtained so that estimates of the coherence length are possible.

Principal Investigator: Peder J. Estrup (Physics and Chemistry).

Personnel: A. Horlacher (Chemistry) and J. W. Chung

(Physics).

Publications: "Desorption Kinetics and Surface Restructuring for H/W(100)", R.A. Barker, A.M. Horlacher, and P.J. Estrup, J. Vac. Sci. Technol. 20 (1982), 536.

"Compatibility of FIM and LEED Observations for the W(100) Reconstruction", P.J. Estrup, L.D. Roelofs and S.C. Ying, Surface Science, in press.

"Two-Dimensional Phases in Chemisorption Systems", L.D. Roelofs and P.J. Estrup, Surface Science, in press.

Supported by the Materials Research Laboratory/NSF and NSF.

Surface Reflectance Spectroscopy (SRS)

As SRS has been shown to reveal information about surface band structure and bonding sites, we have established a new approach which incorporates SRS to understand the electronic properties of materials. The material under investigation is placed in an ultrahigh vacuum system, and is investigated in the clean and chemisorbed state with and without a strong electric field applied perpendicular to the surface. The application of this electric field is accomplished by preparing a transparent insulating solid with a semi-transparent electrode on it which is held near, but off the surface by insulating posts, a few microns high. The data one obtains are equivalent to electroreflectance or modulation spectroscopy with and without a chemisorbed layer. We expect to study materials to which one may apply an electric field; that is, semiconductors, metals, and some marginally conducting "insulators".

Principal Investigators: P.J. Estrup (Physics and Chemistry) and P.J. Stiles (Physics).

Personnel: B.D. Parker (Physics) and J. Prybyla (Chemistry).

Supported by the Materials Research Laboratory/NSF.

Surface Complex Models at Metal Centers in Ionomers

The formation of isolated metal ions or atom-clusters in ionic domains in PSSA and PFSA ionomers permits studies of reactions of small molecules with these types of metal sites to help develop an understanding of the bonding and structure of chemisorbed species. Previous work with Rh and Ru ions and Pd- and Pt-based clusters in PFSA have shown that complexes form with CO, NO, C_2H_2 , and reduction occurs with H_2 and with CO and H_2O . In this year two types of reaction have been achieved. In the first it was shown that thermally induced reductive deamination of $Pt(NH_3)_4^{+2}$ and $Pd(NH_3)_4^{+2}$ occurs in PFSA to form M^0 clusters with regeneration of the H-PFSA and release of NH_3 and N_2 , to produce metal clusters in the ionomer. This system forms carbonyls and functions catalytically for exchange and water gas shifts. The formation of Rh and Ru PSSA ionomers was achieved, its reactions with CO, NO and alcohols examined, and reduction with H_2 and with CO and H_2O achieved. The ion-motion spectra of alkali metal PSSA ionomers, and evaluation of the ion-site forces have been completed.

Principal Investigator: W.M. Risen, Jr. (Chemistry).

Personnel: V.D. Mattera, Jr. (Chemistry) and S.U. Noor (Chemistry).

Publication: "Ionic Interactions in PSSA Ionomers", V.D. Mattera, Jr. and W.M. Risen, Jr., J. Poly. Sci., to be submitted (1982).

Supported by the Materials Research Laboratory/NSF and ONR.

SECTION 5

Lower Dimensionality Materials and Structures

Individual Contributions

Thin Liquid Crystal Films

We have completed a mean field study of the order parameter behavior in thin liquid crystal films below the smectic C-A transition. Our theoretical model is applicable to experiments that have been carried out on films with 2-10 layers and bulk samples. Using one adjustable parameter we have obtained excellent quantitative agreement with the experimental data for films of 2-5 layers and the bulk sample. For films consisting of about ten layers, the agreement between theory and experiment is qualitative and we are considering various physical mechanisms to explain the discrepancy.

Principal Investigator: R. A. Pelcovits (Physics).

Personnel: S.W. Heinekamp (Physics).

Publications: "Order Parameter Behavior in Thin Liquid Crystal Films", E. Fontes, R. Pindak, S. Heinekamp and R.A. Pelcovits, submitted to Phys. Rev. Letts.

Supported by the Materials Research Laboratory/NSF.

Electronic Properties of Semiconducting Surface Space Charge Layers

Because the ellipsoidal energy surfaces in the conduction band of silicon are quite anisotropic, inversion layers on Si(111) and S(110) surfaces have considerably different optical properties than on Si(100) surfaces. We have studied the linear response, including the diffusion current effects, the optical absorption and collective modes on these surfaces. The discrepancy between our calculations and experiment indicates that the standard model of surface inversion layers is omitting something of importance.

We have also studied the intrasubband collective modes of a superlattice of quantum wells in a semiconductor.

Principal Investigator: J.J. Quinn (Physics).

Personnel: K.S. Yi (Physics).

Publications: "Collective Excitations in Semiconductor Superlattices", S. DasSarma and J.J. Quinn, Phys. Rev. B25 (1982), 7603.

"Linear Response of a Surface Space Charge Layer in an Anisotropic Semiconductor", K.S. Yi and J.J. Quinn, submitted to Physics Rev.

"Optical Absorption and Collective Modes of Surface Space Charge Layers on Anisotropic Semiconductors", K.S. Yi and J.J. Quinn, submitted to Phys. Rev.

Supported by the Materials Research Laboratory/NSF and the Office of Naval Research.

Lower Dimensional Systems

Our investigation of the Bethe Ansatz for 1D systems has been extended to include a more general analysis of completely integrable lower dimensional systems in which there has been great recent interest. The Bethe Ansatz seems to be connected to these by the Star-triangle (or the Yang-Baxter) relations. We believe that this leads to the result that the physics of 1+1 or 2D systems is described completely by order-disorder variables and various symmetries. In the 1+1 or 2-dimensional world order-disorder variables may very well be the unifying features that explain the strong similarity between 1+1 dimensional field theories and 2-space dimensional statistical mechanics.

Principal Investigator: Leon N Cooper (Physics).

Publication: "Lower Dimension Completely Integrable Systems" (with E. Berkan), B.W. Lee Memorial Lectures II, Seoul, Korea (1982).

Supported by the Materials Research Laboratory/NSF.

MOSFETS in Semiconductors other than Si

Our electronic industries rely heavily on the technical expertise necessary to utilize the properties of the Si/SiO_x system. We believe that this system should be the paradigm for other semiconductor/semiconductor native oxide systems. We are fashioning MOSFET structures on GaAs, InP and Ge. We have shown that we can obtain passivation, and are now evaluating which method of making source regions is best for our purposes.

Principal Investigator: P.J. Stiles (Physics).

Personnel: E. Crisman (Engineering) and J-I Lee (Physics).

Supported by the Materials Research Laboratory/NSF and the Office of Naval Research.

Electronic Properties of Two-Dimensional Systems (EP2DS)

We are attempting to elucidate the electronic properties of electrons (holes) in dimensionally restricted situations. The bulk of those studies are of electrons in the inversion layers in MOSFET structures.

We have fashioned a system to examine the high source-drain electric field effects of low temperatures. The rise time of our present system is a few nanoseconds. The structures we designed are both short (2 μm) samples which will have a contribution from end effects (as other people have had) and long samples (10 to 20 μm) which have side probes for both the inversion layer and the semi-resistive gate. As we will apply a voltage along the gate as well as the channel, we should not be bothered by an inhomogeneous channel as all other experiments have been. The samples will appear momentarily.

The thermoelectric effect allows one to study other aspects of the electronic properties, namely the properties of the electrons off the Fermi surface shell. We have observed

such at liquid helium temperatures with and without a magnetic field, and are continuing our work on the subject.

The quantized Hall effect has already been utilized as a probe of fundamental constants and will be used as an in-house resistance standard. The theories, to date, which attempt to explain its universality, fall short. There appears to be many reasons for which small perturbations should limit its applicability. We are investigating the effect of probes, contacts, etc.

The de Hass-van Alphen oscillations, being a magnetic property of the electrons is derivable from the free energy, and is not a kinetic effect. We have initiated a program to look for this in Si MOSFET, and have observed a weak signal. Work continues.

Principal Investigator: P.J. Stiles (Physics).

Personnel: P. Smith (Physics), D. Syphers (Physics), and R. Zeller (Engineering).

Supported by the Materials Research Laboratory/NSF in the central facilities, the National Science Foundation, and in past as part of joint studies with IBM (F.F. Fang).

Low Dimensional Quantum Fields and Electronic Disorder

We continue the study of localization problems. In particular, further investigation of 2-d disordered systems subject to a magnetic field led us to the conclusion that electrons delocalize. That is, we find that a given electronic state ($T=0$) does not contribute to the diagonal components σ_{xx} of the conductivity tensor (as described by a $U(m,m)/U(m) \times U(m)$ σ -model) whereas it does contribute to the Hall conductivity σ_{xy} . We continue the work as it may lead to a better understanding of the quantized Hall effect.

Principal Investigator: A.M.M. Pruisken (MRL).

Publication: "Electron (de-) localization in magnetic fields", to be submitted to Phys. Rev. B.

Supported by the Materials Research Laboratory/NSF.

Optical Transformations in M-TCNQ Films

In the investigation of the mechanism of electric field-induced transformations of CuTCNQ and AgTCNQ films by laser Raman spectroscopy, it was discovered that visible light above a threshold level and electron-beams cause partial or complete transformations. The partial transformations yield materials containing M and TCNQ⁰ as well as MTCNQ that are spectroscopically identical to the low impedance material produced by electrical switching. The optical transformation is spontaneously reversible and exhibits memory phenomena. The complete transformations involve continuous irradiation above the threshold until only M⁰ and TCNQ⁰ are formed, and, when carried out under conditions under which TCNQ⁰ can be removed by sublimation, only M⁰ remains in the irradiated region of the film. This direct phototransformation produces well-defined images with high resolution. Electron microscopic production and examination shows that submicron crystalline metal particles can be obtained in exposed regions. The nature of the optical transformations, including their dependences on wavelength, have been investigated.

Principal Investigator: W.M. Risen, Jr. (Chemistry).

Personnel: E.I. Kamitsos (Chemistry).

Publication: "Optically Induced Transformations of Metal TCNQ Materials", E.I. Kamitsos and W.M. Risen, Jr., Solid State Comm., in press, (1982).

Supported by the Materials Research Laboratory/NSF and ONR.

Resonance Raman Study of MTCNQ (M=Cu,Ag) Films and Crystals

Since CuTCNQ and AgTCNQ films were discovered to be optically transformed to M and TCNQ⁰, the nature of the electronic excitations and vibrational electronic interactions in these systems was investigated by resonance Raman spectroscopy. The resonance enhancements were shown to be selective and differ between the low energy and charge

transfer band systems. Based on the normal coordinate analysis of TCNQ and its anions, molecular orbital calculations, and resonance Raman theory, the frequencies and resonance enhancements were computed. The substantial agreement of the calculated and observed resonance Raman spectra for Ag vibrational modes support interpretation of the mechanism for optical transformation.

Principal Investigator: William M. Risen, Jr. (Chemistry).

Personnel: E.I. Kamitsos (Chemistry).

Publication: "Resonance Raman Spectra of CuTCNQ and AgTCNQ Films and Crystals", E.I. Kamitsos and W.M. Risen, Jr., J. Ramen Specty, (1983).

Supported by the Materials Research Laboratory/NSF and ONR.

Instantons and Disordered Systems

We have continued our work on disordered systems. It is now generally agreed that the electronic states of a noninteracting disordered two dimensional system (as found in MOSFETS) are localized. The observation of the quantized Hall effect has stimulated attempts to understand the nature of the states in a quantizing magnetic field. We have shown that the problem can be mapped onto a unitary nonlinear model. The bare coupling constant of the model in the (C.P.A.) is the longitudinal conductance. We predict that the longitudinal conductance of an infinite two dimensional disordered system should be zero. It is important to realize that this result does not imply that the electronic states are localized (at least in the usual sense) as the transverse conductivity is unaffected. We cannot make any direct statements regarding the Hall steps which occur when Fermi level lies in between Landau sub-bands where the theory does not apply. However, we have shown that a disordered electronic system in high magnetic fields can support a finite σ_{xy} when $\sigma_{xx} = 0$. One might speculate that the theory does account correctly for the rise in Hall conductance between steps and the steps come about as σ_{xy} is unchanged as electrons fill localized states in the band tails.

Principal Investigator: A. Houghton (Physics).

Personnel: J. Senna (Physics) and F. Seco (Physics).

Publications: "The Effects of a Random Symmetry Breaking Field on Topological Order in Two Dimensions", A. Houghton, R.D. Kenway and S.C. Ying, Phys. Rev., B23 (1981), 298.

"Thermoelectric Power in a Disordered Two Dimensional Interacting Electron Gas", A. Houghton, J.R. Senna and C.S. Ting), Surf. Sci., 113 (1982), 244.

"Magnetoresistance and Hall Effect of a Disordered Interacting Two Dimensional Electron Gas", A. Houghton, J.R. Senna and S.C. Ying, Surf. Sci., 113 (1982), 520.

"Thermoelectric Power in a Disordered Two Dimensional Electron System", A. Houghton, C.S. Ting and J.R. Senna, Phys. Rev., B25 (1982), 1439.

"Magnetoresistance and Hall Effect of a Disordered Interacting Two Dimensional Electron Gas", A. Houghton, J.R. Senna and S.C. Ying), Phys. Rev., B25 (1982), 2196.

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"Diffusion of Electron in Two Dimensions in Arbitrarily Strong Magnetic Fields", A. Houghton, J.R. Senna and S.C. Ying, Phys. Rev., B25 (1982), 6468.

"Field Theoretic Treatment of the 2d Planar Model with Random p-Fold Symmetry Breaking Field", A. Houghton and Y.Y. Goldschmidt, Nuc. Phys. B210 (1982), 155.

Supported by the Materials Research Laboratory/NSF.

SECTION 6

Properties of Materials at Low Temperatures

Individual Contributions

Plastic Deformation and Ultrasonic Attenuation in Solid Helium-Four

We have previously reported on studies of the deformation of solid helium under conditions of rapid compression and decompression. Such deformation was found to be followed by quasi-periodic changes of ultrasonic attenuation in time, with a period of about 1 minute. The observed behavior was attributed to interference between waves reflected from two interfaces whose separation changes in time. One of these interfaces is stationary (in this case the face of a piston used to produce the deformation), while the other interface is assumed to be moving in a direction perpendicular to the stationary one. Under these conditions we can calculate the required acoustic impedance mismatch for the media involved in order to account for the observations. We have thus found that the properties of the helium layer in contact with the piston would have to differ considerably from those of bulk helium if the experimental observations are due to interference. Further studies are in progress.

Principal Investigator: C. Elbaum (Physics).

Personnel: A. Hikata (Applied Mathematics), J. Beamish (Materials Research Laboratory), M. Manning (Physics).

Supported by the Materials Research Laboratory/NSF.

Atomic Hydrogen at Low Temperatures

Work is proceeding along two lines of research on atomic hydrogen. Firstly, because of difficulties encountered in trying to observe directly the nuclear resonance of gaseous atomic hydrogen at low temperatures and high magnetic fields, we have shifted our approach to the study in the change in density as a function of time as measured with a

pressure cell on saturating the nuclear resonance transition. Since the inception of work on this technique another group has shown it to be highly useful in studying relaxation and recombination processes. Secondly, atomic deuterium is being studied to attempt to understand the very rapid recombination rates observed of atoms bound to the surface of liquid helium. While the measured binding energies appear in agreement with theory, the recombination rates are orders magnitude higher than expected. We have observed atomic deuterium in our 9GHz spectrometer below 1°K and are in the process of measuring the magnitude and temperature dependence of the recombination rates.

Principal Investigator: George Seidel (Physics).

Personnel: R. Mayer (Physics).

Supported by the National Science Foundation.

Properties of the Interface Between Liquid and Solid Helium-4

The interface between liquid and solid helium is of special interest. It is a liquid-solid phase boundary which can exist even in the limit as the temperature $T \rightarrow 0$. The interface is characterized by a very high degree of perfection, and by the absence of impurities. In addition, for low enough temperatures the entropies of the liquid and the solid become very small, and one may view the freezing process as the adiabatic transformation (in the Ehrenfest sense) of one quantum mechanical state into another. Thus, under these conditions melting and freezing is a perfectly reversible quantum mechanical process. We have studied this melting and freezing for ^4He , using high-frequency phonons as a probe of the kinetics of the interface. The results have confirmed the picture described above, and have shown that coherent melting and freezing can occur even on very short time scales.

Principal Investigator: H.J. Maris (Physics).

Personnel: T. Huber (Physics).

Publications: "Kapitza Resistance Between Liquid and Solid

Helium. I. Theory", J. Low Temp. Phys., 48 (1982), 99.

"Kapitza Resistance Between Liquid and Solid Helium. II. Experiment, J. Low Temp. Phys., 48 (1982), 463.

Supported by the Materials Research Laboratory/NSF and the National Science Foundation.

Heat Transport in Dielectric Glasses

We have been studying the thermal conductivity K of dielectric glasses at low temperatures. At temperatures between 1 and 10K nearly all dielectric glasses, and many other amorphous materials, have a temperature-independent thermal conductivity, or "plateau" regime. In this temperature range the phonon mean-free-path as deduced from thermal conductivity measurements is extremely short, and we have been investigating the possibility that relevant phonons are in fact localized in the Anderson sense. To do this we have developed a numerical technique for finding the vibrational modes of disordered systems, and we will apply this to various mechanical models of glasses.

Principal Investigator: H.J. Maris (Physics).

Personnel: M. Williams (Physics).

Supported by the Materials Research Laboratory/NSF.

Properties of Helium in Porous Vycor Glass

We have begun construction of an apparatus to measure the specific heat of solid helium in porous vycor glass. The apparatus is able to measure the specific heat at temperatures in the range 0.06K to 4K, and for pressures up to 100 Bars. The pores in our vycor glass are approximately 60 \AA in diameter. Because of the irregular shape of the pores, we expect that many of the solid helium atoms will be in "non-crystalline" configurations. The tunneling motion of these atoms will lead to a specific heat contribution which is linear in T , as is observed in most noncrystalline materials at low temperatures.

Principal Investigator: H.J. Maris (Physics).

Personnel: J.L. Wilson (Physics).

Supported by the Materials Research Laboratory/NSF.

SECTION 7

Materials for Solar Energy Conversion

Individual Contributions

Hydrodesulfurization Catalysts

Magnetic Properties of Bulk and Supported Co_9S_8

The nature of the cobalt present in sulfided cobalt molybdate catalysts has been the subject of several studies. An early study by deBeer indicated that the sulfur content present in sulfided cobalt molybdate catalysts corresponded to the value anticipated for a composition of Co_9S_8 and MoS_2 . However, the actual catalysts are amorphous, and a discrete Co_9S_8 phase has never been observed in $\gamma\text{-Al}_2\text{O}_3$ supported systems within the composition range of commercial interest.

Since magnetic susceptibility appears to be capable of distinguishing the various members of the Co-S and Co-O systems, it was decided to compare the magnetic properties of Co_9S_8 made by direct combination of the elements with those obtained from sulfurizations of both bulk $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and cobalt sulfate dispersed on a $\gamma\text{-Al}_2\text{O}_3$ support. The magnetic susceptibility of sulfurized cobalt sulfate on $\gamma\text{-Al}_2\text{O}_3$ shows a marked temperature dependency, which is in contrast to the susceptibility of bulk Co_9S_8 made under identical conditions. This difference may, therefore, be attributed to some chemical interaction with the substrate. Although the Curie constant and effective moment for the supported sample differ from those reported for CoAl_2O_4 , nevertheless, the observation of a temperature-dependent magnetic susceptibility is evidence for the presence of some cobalt in an oxygen environment in addition to the existence of Co_9S_8 .

Preparation and Properties of the Systems $\text{Co}_{1-x}\text{Ru}_x\text{S}_2$ and $\text{Rh}_{1-x}\text{Ru}_x\text{S}_2$

Synthesis of members of the $\text{Co}_{1-x}\text{Ru}_x\text{S}_2$ and $\text{Rh}_{1-x}\text{Ru}_x\text{S}_2$ has been accomplished by the sulfurization of mixtures of $(\text{NH}_4)_2\text{RuCl}_6$ and $\{\text{Co}(\text{NH}_3)_5\text{Cl}\}\text{Cl}_2$ or $(\text{NH}_4)_2\text{RuCl}_6$ and $(\text{NH}_4)_3\text{RhCl}_6$. The magnetic properties of these systems are dependent on the degree of localization of the 4d electrons. From comparison with the system $\text{Co}_{1-x}\text{Rh}_x\text{S}_2$, it appears that the 4d electrons of $\text{Rh}(4d^7)$ are localized in the presence of $\text{Co}(3d^7)$ but delocalized in the presence of $\text{Ru}(4d^6)$. Members

of these systems are difficult to prepare as single homogeneous products, but magnetic susceptibility measurements can be used to determine when such products are obtained.

Photoelectrolysis

Structural and Electronic Relationships between Conducting Iron Niobates and Iron Tungstates

A number of ternary iron oxides have been prepared and their electronic properties have been determined. They crystallized in a number of related structures, and differences in the arrangement of the transition metal cations can be related to the observed conductivities. The structures studied were the wolframite, tri- α - PbO_2 and columbite, which represent ordered variants of the basic α - PbO_2 type. When FeNbO_4 crystallizes with the wolframite structure, the Fe and Nb cations are arranged in an ordered manner which results in the lowering of the symmetry from orthorhombic to monoclinic. As in α - PbO_2 , there are formed zigzag chains of $\{\text{FeO}_6\}$ and $\{\text{NbO}_6\}$ octahedra, but each chain contains only either Fe or Nb. The same structural features have been observed for the composition of FeWo_4 . These compounds can accommodate both divalent and trivalent iron in the zigzag chains of $\{\text{FeO}_6\}$ octahedra, which results in high conductivity because of the electron transfer within these chains. Two other variants of the α - PbO_2 type are the tri- α - PbO_2 and the columbite structures. For these variants, there is a 2:1 cation ordering rather than the 1:1 order observed in the wolframite structure. FeNb_2O_6 has the columbite structure, and Fe_2Wo_6 can be prepared as a single phase with the tri- α - PbO_2 structure. The existence of mixed iron valencies in the Fe-Nb-O phases has been shown to be due to the solid solution of FeNbO_4 and FeNb_2O_6 . There is also evidence for the solid solution between FeWo_4 and Fe_2Wo_6 . Undoubtedly, the existence of both Fe^{2+} and Fe^{3+} in these zigzag chains is the basis for the observed conductivity.

Principal Investigator: A. Wold (Chemistry).

Personnel: K. Dwight (Chemistry), R. Kershaw (Chemistry), B. Khazai (Chemistry), K. Kim (Chemistry), W. Croft (Chemistry), H. Leiva (Chemistry), K. Sieber (Chemistry), J. Covino (Chemistry), M. Tellefsen (Chemistry), D. Passquariello (Chemistry), J. Foise (Chemistry), J. Marzik (Chemistry), K. Kourtakis (Chemistry).

Publications: "Electroreflectance and Reflectance Study of $2H-MoSe_2$ ", P. Amirtharaj, F. Pollak, and A. Wold, Solid State Communications 41 No. 8 (1982), 581.

"Preparation and Characterization of Conducting Iron Tungstates", H. Leiva, K. Dwight, A. Wold, J. Solid State Chemistry 42 (1982), 41.

"Magnetic Properties of Dispersed Nickel Particles on Spherocharb", K. Kim, R. Kershaw, K. Dwight, A. Wold, Mat. Res. Bull. 17 (1982), 591.

"Preparation and Properties of the System $Co_{1-x}Rh_xS_2$ ", J. Covino, K. Dwight, A. Wold, R. Chianelli, J. Passaretti, Inorganic Chemistry, 21 (1982), 1744.

"Preparation and Photoelectronic Properties of $FeWO_4$ ", K. Sieber, K. Kourtakis, R. Kershaw, K. Dwight, A. Wold, Mat. Res. Bull. 17 (1982), 721.

"Characterization of n-Type Semiconducting Tungsten Disulfide Photoanodes in Aqueous and Nonaqueous Electrolyte Solutions", J. Baglio, G. Calabrese, E. Kamieniecki, R. Kershaw, C. Kubiak, A. Ricco, A. Wold, M. Wrighton, G. Zoski, J. Electrochem. Science and Technology, 129, No. 7 (1982), 1461.

"Structural and Electronic Relationships between Conducting Iron Niobates and Tungstates", H. Leiva, K. Sieber, B. Khazi, K. Dwight, A. Wold, J. Solid State Chemistry, 44 No. 1, (1982).

"Preparation and Properties of PdPSe Single Crystals", J. Marzik, R. Kershaw, K. Dwight, A. Wold, J. Solid State Chemistry, 44 No. 3, (1982).

"Magnetic Properties of Bulk and Supported Co_9S_8 ", J. Covino, K. Kim, D. Passquariello, K. Dwight, A. Wold, Mat. Res. Bull., 17 No. 9, (1982).

"Preparation and Properties of the Systems $Co_{1-x}Ru_xS_2$ and $Rh_{1-x}Ru_xS_2$ ", J. Foise, K. Kim, J. Covino, K. Dwight, A. Wold, Inorganic Chemistry, to be published.

Supported by Materials Research Laboratory/NSF, the National Science Foundation, the Office of Naval Research, Exxon Research and Engineering, and General Telephone Laboratories, Inc.

Semiconductor Powder Processing for Photovoltaic Cells

This program is concerned with the fabrication and characterization of large grained compacts of alloys of the copper ternary semiconductors like CuInSe_2 , CuInS_2 , etc. The potential of these materials for the fabrication of extremely low cost photovoltaic cells is high, since conversion efficiencies of 9.5% have been achieved by other fabrication techniques using them in heterojunction cells with CdS. Our powder compact cells, as well as those fabricated by others, appear to be remarkably stable or even to improve with time during storage in air at room temperature.

Our activities on this program during the past year have been mainly focused on characterization. In particular, we have completed the design and construction of a cathodoluminescent attachment for the AMR scanning electron microscope in the Brown MRL Electron Microscopy Facility. This equipment is to be used for characterization work on the semiconductor materials being used in this program, as well as others, for fabrication of solar cells. Construction of the equipment began during the summer after the arrival of Visiting Professor T. Warminski from the Polish Academy of Sciences. Assembly, installation and initial testing of room temperature operation was completed in early summer of 1982. The main optical component of the device is a half-ellipsoidal mirror which is used to enhance the collection of the cathodoluminescent light generated in the semiconductor specimen when irradiated by the scanning electron beam of the microscope. The specimen to be examined is located at one focus of the mirror and a lens and fiber optic bundle at the other. The cathodoluminescent signal, which is generated in synchrony with the scanning electron beam, is passed through the vacuum chamber to an external grating monochromator for wavelength analysis. Initial tests of the system have established the required assembly techniques and the operational characteristics of the components selected. Cathodoluminescent images have, so far, been recorded only for the integrated signals without wavelength analysis. It is expected that observations of localized variations in wavelength (and energy gap) will require cooling of the specimen as well as additional work on the design of equipment which can be accommodated in the SEM chamber.

A small effort was also devoted to fabrication and testing of photovoltaic cells. In particular, cells were fabricated on specimens of two pentenary alloys using a CdS evaporation procedure which had been optimized during a series of control experiments by R. Arya. This procedure is based on the use of CdS which is deficient in sulfur by approximately 2% of a source temperature of 1000 to 1050°C, and a

substrate temperature of 150-175°C. The cells under simulated AMI illumination showed much improved characteristics compared to those fabricated previously. In particular, for a cell of $\text{CuIn}_{0.3}\text{Ga}_{0.7}\text{Se}_{1.2}\text{Te}_{0.8}$, we observed $I_{\text{SC}}=32 \text{ ma/cm}^2$, $V_{\text{oc}}=0.32 \text{ volt}$, $\text{F.F.}=0.56$, and $\text{Efficiency}=5.71\%$; for a cell of $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{SeTe}$, $I_{\text{SC}}=29.5 \text{ ma/cm}^2$, $V_{\text{oc}}=0.39 \text{ volt}$, $\text{F.F.}=0.53$ and $\text{Efficiency}=6.1\%$. Improvements in performance are due to the low resistivity of the CdS films and in improved technique. Although large short circuit current densities are achieved, improvements in open circuit voltage require increased attention to the reduction of the density of interfacial sites.

Principal Investigators: B. Roessler (Engineering), J.J. Loferski (Engineering), and J. Gurland (Engineering).

Personnel: T. Warminski (Engineering), M. Kwietniak (Engineering), R. Arya (Engineering), U. Schwuttke (Engineering), P. Delzio (Engineering), W. Oates (Engineering).

Supported by the Materials Research Laboratory/NSF.

Investigation of Photovoltaic Solar Cells

This program continues to explore solar cells based on ternary chalcopyrite semiconductors like CuInSe_2 and their alloys {e.g. $\text{CuIn}_y\text{Ga}_{1-y}\text{Se}_{2z}\text{Te}_{2(1-z)}$ }; thermophotovoltaic cells based on germanium, and heterojunction cells in which CdS is the wide band gap n-type window material and the photovoltaically active absorber semiconductors are Si or CdTe.

The most promising activity is that which resulted in efficient cadmium sulfide on silicon solar cells. Thin films of low resistivity ($\rho \sim 0.01 \text{ ohm cm}$) CdS were sputtered over single crystal p-Si wafers. The CdS films were polycrystalline and predominantly hexagonal, as indicated by x-ray diffraction. Their transmittance over the solar spectrum (0.5μ to 2.0μ) was about 82 percent for a 5.2 micron thick film and about 86 percent for a 2.7 micron thick film. The CdS layer was produced by evaporation Cd enriched CdS (source temperature 1050-1100°C) onto the silicon maintained at temperatures in the 150°C to 200°C range). The best of these devices had a simulated AMI solar illumination conversion efficiency of 11.1 percent for cells having an area of 1 cm^2 . There certainly is a silicon oxide

layer between the Si and the CdS so that the possibility existed that we had an S-I-S structure similar to the indium-tin oxide /silicon oxide/ silicon cell and tin oxide /silicon oxide/ silicon cell. However, analysis of the temperature dependence of the current-voltage characteristics of these devices showed that the forward current can be described by a multi-step tunneling mechanism governed by the equation:

$$J = J_0 \exp BV$$

where B is independent of temperature and

$$J_0 = J_\infty \exp T/T_0$$

This is to be contrasted with the current-voltage dependence of a classical p/n homojunction for which the forward current has the form:

$$J = J_0 \exp(qV/kT).$$

and

$$J_0 \propto \exp(-E_G/kT).$$

There is a large (~4%) lattice mismatch between CdS and Si and it is therefore very interesting that devices having such good photovoltaic characteristics should result from bringing these semiconductors together.

During the year, we were able to improve our ability to characterize the composition of our thin films by energy dispersive analysis of x-rays (EDAX) and wave dispersive analysis of x-rays (WDX) in the MRL Central Facility for Electron Microscopy. Dr. T. Warminski of the Institute of Physics of the Polish Academy of Sciences, Warsaw, spent a year at Brown and introduced new methods for analyzing the EDAX and WDX data. These new methods were used to study the low resistivity CdS films deposited by evaporation on various substrates. To our surprise, EDAX analysis indicates that the films are sulfur rich; their sulfur content ranged between 50.2 at. % and 51.5 at. % for films with resistivities between 0.1 and 0.01 ohm cm. The powder charge which was evaporated to produce these films was CdS and had a composition of S = 49.5%, Cd = 50.5%. Careful exploration of this phenomenon involving calibration of the EDAX system led to the conclusion that all of the CdS films deposited by evaporation of sulphur deficient CdS powder turned out to be sulfur rich. This matter is under continuing investigation since sulfur-rich CdS should not have low resistivity.

In another development, we have reactivated an alternate way to deposit CdS, namely by open-tube chemical vapor transport

with pure hydrogen as the transporting agent. In this technique, a boat containing CdS is placed in a hot zone in an open tube furnace and the substrate in a zone where the temperature can be maintained between 500 and 700°C. The hydrogen can be passed through the tube in either direction. It is first passed over the substrate in order to clean the surface of oxides and any adsorbed gases. After a pre-selected cleaning time, the direction of hydrogen flow is reversed so that it passed over the CdS first. The CdS is thus deposited on a freshly cleaned surface. We have been seeking a method to control the interface between the CdS and the substrate to explore the role of interfacial states. Evaporation of CdS onto a substrate in a standard evaporator must almost invariably result in an oxide layer between the two semiconductors. Initial experiments have involved depositing CdS over single crystal grains of CuInSe_2 obtained from Dr. W. Giriat of the Venezuelan Institute for Scientific Research (IVIC) in Caracas, Venezuela. (The Brown Photovoltaic Research Group has an NSF sponsored cooperative research program with Dr. Giriat's group at IVIC). It was found that the CdS layer can become copper doped in this deposition method. This suggests that there may be some decomposition of the near surface layers of the CuInSe_2 crystal grain.

In the thermophotovoltaic (TPV) area, we obtained a sample of Ge + 4% Si deposited by CVD onto a GaAs single crystal by chemical vapor deposition of a mixture of germane and silane. This structure should be a minority carrier mirror and the control of the reverse saturation current of p/n junctions with the help of minority carrier mirrors will be studied in it.

During this year we finished construction of a new thin film facility which includes an MRC rf-sputtering system. A GaAs target has been purchased and thin films of GaAs suitable for solar cells and other applications are being deposited with this system.

Principal Investigators: Joseph J. Loferski (Engineering) and B. Roessler (Engineering).

Personnel: G. Kenshole (Engineering), T. Warminski (Engineering), M. Kwietniak (Engineering), E. Crisman (Engineering and Physics), R. Beaulieu (Engineering), W. Oates (Engineering), P. Sarro (Engineering), R. Arya (Engineering), C. Cose (Engineering), G. Doodlesack (Engineering), Y. Ercil (Engineering), E. Vera (Physics) and L. Susani (Engineering).

Publications: "Operating Characteristics of Thin

Thermophotovoltaic Cells with Minority Carrier Mirrors and Optical Mirrors Using Selective Radiators of Erbium and Ytterbium Oxides", E.S. Vera, J.J. Loferski and M. Spitzer, Proceedings of the Fourth European Communities International Conference on Photovoltaic Solar Energy Conversion, Stresa, Italy (May 1982), 659-665.

"Thin Film Heterojunction CdS/Cu Ternary Alloys Solar Cells with Minority Carrier Mirrors", M. Kwietniak, J.J. Loferski, R. Beaulieu, R.R. Arya, E.S. Vera and L. Kazmerski, Proceedings of the Fourth European Communities International Conference on Photovoltaic Solar Energy Conversion, Stresa, Italy (May 1982), 727-731.

"Thin Film Heterojunction Solar Cells Based on n-CdS and p-Cu Ternary Alloys", J.J. Loferski (invited), Proceedings of the International Workshop on the Physics of Semiconductor Devices, (New Delhi, India, November 1981).

"Efficient Cadmium Sulfide on Silicon Solar Cells", R.R. Arya, P.M. Sarro and J.J. Loferski, Appl. Phys. Lett. 41 (August 1982), 355-357.

Supported by the Materials Research Laboratory/NSF, SERI, U.S. Department of Energy, Amperex Corporation, NRL, Standard Oil of Ohio, and the Mobil Oil Foundation.

SECTION 8

Other Research

Individual Contributions

Collapse Problem in Rubber Elasticity

The theory of rubber elasticity is based on the consideration of an amorphous network of cross-linked long-chain molecules. If all atomic interactions apart from the covalent interactions between neighboring backbone interactions of a given chain are neglected, then the theory predicts that the network configuration which corresponds to zero applied load is one in which the entire network contracts to a single point. This defect in the theory is referred to as the collapse problem.

We have reconsidered the statistical mechanical formulations of rubber elasticity, particularly with regard to the treatment of interactions between atoms of the network which are not covalently-bonded to each other. In our formulation these are represented as a sum of two potentials: (i) a deformation-dependent one-body potential and (ii) a deformation-independent two-body potential. The first gives rise to an internal pressure while the second represents the remaining excluded-volume effects. We find the first is more important in preventing network collapse than the second.

A simple atomistic model has been developed to illustrate these ideas and the model has been studied by computer simulation by the method of Brownian dynamics. The model also has relevance for the problem of a tie molecule between two parallel lamellae in a semi-crystalline polymer.

Principal Investigator: J. H. Weiner (Engineering).

Personnel: T. W. Stevens (Engineering).

Publication: "Relative Importance of Internal Pressure and Excluded-Volume Effects in Resolution of Network Collapse

Problem," J.H. Weiner and T.W. Stevens, submitted to Macromolecules.

Supported by the Materials Research Laboratory/NSF and the Gas Research Institute.

Picosecond Spectroscopy of Semiconductors

Picosecond optical methods have been used to excite and probe electronic excitations near the lowest interband transitions in crystalline semiconductors. As a continuation of work in the narrow-gap materials, excited state lifetimes and some dielectric properties have been examined in a high density electron-hole plasma for $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$. This alloy, where the bandgap can be varied over a wide range of infrared wavelengths, has been previously shown to possess a strong nonradiative Auger recombination channel for nondegenerate electron densities at moderate temperatures. Our work has examined the recombination at excess densities up to and exceeding $1 \times 10^{19} \text{ cm}^{-3}$. It is found that while still dominating the recombination, the strength of the Auger process is much reduced, evidently due to effective plasma screening. Elsewhere, we have applied pico-second optical modulation methods to examine transient band exciton effects in $\text{Ga}_{1-x}\text{In}_x\text{P}$ ($x=.50$). Here, much in contrast with expectations based on steady-state photoluminescence data, strong electron-phonon coupling is evident shortly following picosecond excitation. Spectral measurements identify this behavior with a short lived acceptor-bound, polaron-like excitation.

Principal Investigator: A.V. Nurmikko (Engineering).

Personnel: J.K. Ajo (Engineering).

Publications: "Some Properties of a High Density Electron-Hole Plasma in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ ", A.V. Nurmikko and B.D. Schwartz, J.Vac. Sci. and Technology 21 (1982), 229.

"Strong Electron-Phonon Interaction Effects in Modulated Transient Reflectance Spectra of $\text{Ga}_{.50}\text{In}_{.50}\text{P}$ ", S. Sugai, J. Harris, and A.V. Nurmikko, Solid State Comm., 43,913 (1982).

Supported by the Materials Research Laboratory, NSF, AFOSR.

Picosecond Studies of Soliton Diffusion in Polyacetylene

Photoinduced dichroism caused by bleaching of the interband transition in trans-(CH)_x was observed in the picosecond time domain. The photoinduced bleaching persists to long time; however, polarization memory is lost after about a nanosecond. From the measurement of the decay of the polarization memory the diffusion constant of the charged excitations was determined ($D \approx 2 \times 10^{-2} \text{ cm}^2 \text{ sec}^{-1}$ at 300 and 80K).

Principal Investigator: Jan Tauc (Engineering and Physics).

Personnel: Z. Vardeny (Engineering) and J. Strait (Physics).

Publications: "Picosecond Photoinduced Dichroism in Trans - (CH)_x: Direct Measurement of Soliton Diffusion", Z. Vardeny, J. Strait, D. Moses, T.-C. Chung and A.J. Heeger, Phys. Rev. Lett., 49 (1982), 1657.

Supported by the Materials Research Laboratory/NSF and NSF.

Ultrasonic Studies of Phase Transitions

Ultrasonic studies of phase transitions were examined from the point of view of the responses of high frequency waves to order parameter changes and of pretransitional fluctuations. Emphasis was given to recent investigations of anharmonic effects in ultrasonic propagation near the lambda transition of liquid helium as an example of the role played by nonlinear properties. In particular, experimental results were reexamined on the diverging behavior of the anharmonic coupling coefficient between the fundamental wave and its second harmonic, as the transition temperature is approached.

Principal Investigator: C. Elbaum (Physics).

Personnel: A. Hikata (Applied Mathematics).

Publication: "Ultrasonic Studies of Phase Transitions",
Journal de Physique, 42 (1981), C5-855.

Supported by the Materials Research Laboratory and NSF.

X-Ray Topography

Our activities on oxidation of zinc employing x-ray topography, together with complementary optical and electron microscopic techniques, were reduced following completion of the doctorate thesis of K.C. Yoo in September. They included analysis of his results and preparation of publications based on his work. This analysis indicates that basal dislocation loops observed by Berg-Barrett X-Ray topography may be influenced by the presence of inclusions incorporated into the crystal during solidification and that loop growth as a result of vacancy injection during room temperature oxidation is influenced by the presence of slip dislocations near inclusions. Stereo imaging of dislocation bundles clarifies interpretation of such dislocation structures and when it is available--as with our Berg-Barrett topography of zinc employing cobalt radiation--provides unique insight into the processes which occur in the crystal lattice. It has also been observed that an extremely high density of basal dislocation loops can be introduced into zinc during chemical polishing of nitric acid. These loops are of nearly constant size and are probably formed along nucleation sources provided by dislocation debris from prior mechanical polishing. Room temperature climb in such a polished crystal produces a dislocation structure of interconnected loops which, if present, can be expected to have significant effects on surface sensitive properties.

X-ray topographic studies resumed in late spring on an exploratory investigation of crystal perfection of germanium for use in solar thermal-photovoltaic devices. In these devices solar radiation is absorbed by and heats a surface which is not susceptible to radiation damage. The solar heated body re-emits at a wavelength which is optimized for absorption by a germanium photovoltaic diode. It is anticipated that characterization work on germanium photovoltaic cells-- as a function of fabrication processing--by x-ray topography and complementary optical and electron microscopic techniques will be expanded next year under a program also supported by the Naval Research Laboratories.

Principal Investigator: B. Roessler (Engineering).

Personnel: K.C. Yoo (Engineering) and W. Oates (Engineering).

Publication: "Reflection X-Ray Topography of Hardness Indentations in Copper Single Crystals", K.C. Yoo, B. Roessler, R. W. Armstrong and M. Kuriyama, Scripta Met., 15 (1981), 1245-1250.

Supported by the Materials Research Laboratory/NSF and NSF.

Lecturers in the Materials Research Laboratory Program,
1981-82

July 9, 1981

Theoretical Seminar: Department of Physics, Professor Moorad Alexanian, Centro de Investigacion del IPN, EXACT SOLUTIONS OF THE BOLTZMANN EQUATION.

July 21, 1981

Many-body Scattering Theory Lecture: Department of Physics, Professor W. Sandhas, Brown and Bonn Universities, THE COULOMB PROBLEM IN QUANTUM COLLISION THEORY.

August 4, 1981

Solid State and Materials Science Seminar: Department of Physics, Professor R. Labusch, Argonne National Laboratory, ELECTRICAL TRANSPORT ALONG DISLOCATIONS IN SEMICONDUCTORS.

August 10, 1981

Inorganic Glass Research Group: Department of Physics, Professor Dr. Werner Vogel, Otto Schott Institute of the Friedrich-Schiller Universitat, ELECTRON MICROSCOPE EXAMINATION OF GLASS.

September 14, 1981

Nuclear Seminar: Department of Physics, Professor M. Bauer, National University of Mexico, A UNIFIED OPTICAL POTENTIAL FOR BOUND AND SCATTERING STATES.

October 1, 1981

Condensed Matter Seminar: Department of Physics, Professor A. Houghton, Brown University, DISORDER, LOCALIZATION, INTERACTION AND ALL THAT.

October 2, 1981

Chemistry Colloquium: Department of Chemistry, Dr. F. Read McFeely, Massachusetts Institute of Technology, PROBING CHEMISORPTION STRUCTURES WITH ANGLE RESOLVED PHOTOEMISSION.

October 5, 1981

Theoretical Lunch Seminar: Department of Physics,

Professor R. A. Pelcovits, Brown University, ANHARMONIC EFFECTS IN '1-DIMENSIONAL SOLIDS'.

October 7, 1981

N-Body Scattering Theory Seminar: Department of Physics, Ms. J. Shertzer, Brown University, ELEMENTS OF THE FINITE ELEMENT METHOD.

October 7, 1981

Solid Mechanics Seminar: Division of Engineering, Dr. David Linton Johnson, Schlumberger-Doll Research, SLOW WAVES IN POROUS MEDIA.

October 8, 1981

Condensed Matter Seminar: Department of Physics, Professor P.J. Stiles, Brown University, REPORT ON THE CONFERENCE OF ELECTRONIC PROPERTIES OF TWO-DIMENSIONAL SYSTEMS (NEW HAMPSHIRE, 1981).

October 9, 1981

Chemistry Colloquium; Department of Chemistry, Dr. Sally Chapman, Barnard College, VIBRATIONAL EFFECTS IN THE REACTION $O_3 + NO_2 + O_2$.

October 13, 1981

Solid Mechanics Seminar: Division of Engineering, Dr. Hermann Riedel, Max-Planck-Institut fur Eisenforschung, CRACK TIP STRESS FIELDS AND CRACK GROWTH UNDER CYCLIC LOADING CREEP CONDITIONS.

October 15, 1981

Condensed Matter Seminar: Department of Physics, Dr. T. Moustakas, Exxon Research Laboratory, ELECTRONIC PROPERTIES OF SPUTTERED HYDROGENATED AMORPHOUS SILICON.

October 15, 1981

Chemistry Colloquium: Department of Chemistry, Dr. William Reinhart, University of Colorado, CLASSICAL, SEMI-CLASSICAL AND QUANTUM VIEWS OF NON-STATISTICAL UNIMOLECULAR DYNAMICS.

October 16, 1981

Partial Differential Equations Seminar: Division of Applied Mathematics, Professor Podio Guidugli, University of Pisa, THE TRACTION PROBLEM IN FINITE ELASTICITY.

October 20, 1981

Solid Mechanics Seminar: Division of Applied Mathematics, Dipl. Ing. Martin Koller, Inst. fur Mech., Zurich, IMPACT OF RIGID SPHERES ON THICK ELASTIC PLATES.

October 21, 1981

Applied Mathematics Seminar: Division of Applied Mathematics, Professor A.C. Pipkin, Brown University, FIBER REINFORCED MATERIALS.

October 21, 1981

Special Seminar: Department of Physics, Dr. I. Binjio, Los Alamos Scientific Laboratory, PHASE CONJUGATE REFLEXION: TIME REVERSAL IN NON-LINEAR OPTICS.

October 22, 1981

Theoretical Seminar: Department of Physics, Prof. C. Rebbi, Brookhaven National Laboratory, MONTE CARLO SIMULATIONS FOR SYSTEMS WITH FERMIONS.

October 22, 1981

Condensed Matter Seminar: Department of Physics, Dr. J. Walker, Massachusetts Institute of Technology, RE-ENTRANT PHASE TRANSITION IN BINARY LIQUID MIXTURES AND LIQUID CRYSTALS.

October 23, 1981

Chemistry Colloquium: Department of Chemistry, Dr. David Chandler, University of Illinois, SIMPLE IDEAS ABOUT THE DYNAMICS OF ELEMENTARY REACTIONS IN LIQUIDS: THE BREAKDOWN OF TRANSITION STATE THEORY.

October 26, 1981

Solid Mechanics Seminar: Division of Engineering, Professor Charles Speziale, Stevens Institute of Technology, MATERIAL FRAME INDIFFERENCE IN GENERALIZED CONTINUUM MECHANICS.

October 26, 1981

Physics Colloquium: Department of Physics, Professor R. Jackiw, Massachusetts Institute of Technology, CHARGE FRACTIONALIZATION IN CONDENSED MATTER AND PARTICLE PHYSICS.

October 27, 1981

Solid Mechanics Seminar: Division of Engineering, Professor C. Polizzotto, Università di Palermo, SHAKEDOWN ANALYSIS AND DESIGN IN PRESENCE OF LIMITED DUCTILITY BEHAVIOR.

October 29, 1981

Condensed Matter Seminar: Department of Physics, Professor S. Nagel, University of Chicago, QUENCHED ECHOES, LOCALIZATION AND ANOMALOUS ANHARMONICITY IN GLASSES.

November 2, 1981

Physics Colloquium: Department of Physics, Professor M. Tinkham, Harvard University, BEYOND EQUILIBRIUM SUPERCONDUCTIVITY.

November 3, 1981

Solid Mechanics Seminar: Division of Engineering, Dr. B. Broberg, University of Lund, FRACTURE MECHANICS: THEORETICAL, EXPERIMENTAL AND APPLIED.

November 4, 1981

Special Condensed Matter Seminar: Department of Physics, Dr. G. Grinstein, IBM Watson Research Center, PHASE TRANSITIONS IN THREE-DIMENSIONAL SYSTEMS WITH COMPETING INTERACTIONS.

November 5, 1981

Joint Theoretical and Condensed Matter Seminar: Department of Physics, Professor R. Zia, Virginia Polytechnic Institute, SURFACE TENSION, EQUILIBRIUM SHAPE AND THE ROUGHENING TRANSITION: EXACT RESULTS FOR THE 2-D ISING MODEL.

November 9, 1981

Physics Colloquium: Department of Physics, Professor R. Donnelly, University of Oregon, QUANTUM TURBULENCE.

November 9, 1981

Joint Lefschetz Center for Dynamical Systems and Solid Mechanics Seminars: Divisions of Applied Mathematics and Engineering, Professor M.E. Gurtin, Carnegie-Mellon University, WAVE PROPAGATION IN MATERIALS WITH MEMORY: THEORY AND EXPERIMENT.

November 10, 1981

Solid Mechanics Seminar: Division of Engineering, Dr. T.X. Yu, Research Institute of Construction Machinery, Tianjin, China, PLASTIC BENDING AND SPRINGBACK OF STRIPS AND PLATES: THEORY, TESTS, AND DESIGN APPLICATIONS.

November 12, 1981

Condensed Matter Seminar: Department of Physics, Dr. A. B. Fowler, I.B.M., CONDUCTANCE IN RESTRICTED DIMENSION ACCUMULATION LAYERS.

November 16, 1981

Physics Colloquium: Department of Physics, Dr. R. Zallen, Xerox Research Laboratories, APPLICATIONS OF PERCOLATION THEORY.

November 17, 1981

Materials Science Seminar: Department of Physics, Dr. Frank Szofran, Mc Donnell-Douglas Research Laboratories, DIRECTIONAL SOLIDIFICATION AND CHARACTERIZATION OF $\text{Hg}_{(1-x)}\text{Cd}_x\text{Te}$.

November 18, 1981

Special Condensed Matter Seminar: Department of Physics, Professor S. K. Ma, University of California--San Diego and IBM, CALCULATION OF ENTROPY FROM A PHASE SPACE TRAJECTORY.

November 19, 1981

Condensed Matter Seminar: Department of Physics, Professor B. Halperin, Harvard University, QUANTIZED HALL CONDUCTANCE.

November 20, 1981

Partial Differential Equations Seminar: Department of Applied Mathematics, Dr. F. Bloom, University of Connecticut, NONLINEAR EVOLUTION EQUATIONS ASSOCIATED WITH NONLINEAR DIELECTRIC PHENOMENA.

November 24, 1981

Numerical Analysis Seminar: Division of Applied Mathematics, Mr. Martin Bendsøe, Brown University, OPTIMIZATION OF PLATES WITH STIFFENERS.

November 30, 1981

Physics Colloquium: Department of Physics, Professor B. Widom, Cornell University, PHASE EQUILIBRIA AND THEIR CRITICAL POINTS.

November 30, 1981

Solid Mechanics Seminar: Division of Engineering, Dr. Gianfranco Capriz, University of Pisa, BALANCE EQUATIONS FOR CONTINUA WITH MICROSTRUCTURE.

December 2, 1981

Special Theoretical Seminar: Department of Physics, Dr. P. Orland, University of California--Santa Cruz, DYNAMICAL DUALITY IN SYMMETRIC GROUP SPIN SYSTEMS.

December 3, 1981

Theoretical Seminar: Department of Physics, Professor M. B. Gavela, Harvard University and LAPP, THE ELECTRIC DIPOLE MOVEMENT OF THE NEUTRON.

December 3, 1981

Condensed Matter Seminar: Department of Physics, Dr. H. Scher, Xerox Webster Research Center, RECOMBINATION PROCESSES IN MOLECULAR SOLIDS.

December 3, 1981

Chemistry Colloquium: Department of Chemistry, Dr. Arthur Sleight, Dupont Chemical Company, MOLYBDATE CATALYSTS.

December 4, 1981

Special Solid State and Electrical Sciences Seminar: Department of Physics, Dr. T. Ohyama, Osaka University, FAR-INFRARED MAGNETO-ABSORPTION OF PHOTOEXCITED SEMICONDUCTORS.

December 7, 1981

Solid Mechanics Seminar: Division of Engineering, Dr. Shigeru Aoki, Tokyo Institute of Technology, ENERGY-RELEASE-RATE IN ELASTIC-PLASTIC FRACTURE PROBLEMS.

December 7, 1981

Physics Colloquium: Department of Physics, Dr. C. Bottcher, Oak Ridge National Laboratory, IONIZATION AND CHARGE EXCHANGE IN ATOMIC PHYSICS.

December 8, 1981

Informal N-body Scattering Theory Seminar: Department of Physics, Dr. C. Bottcher, Oak Ridge National Laboratory, ION-ATOM COLLISIONS.

December 9, 1981

Nuclear Seminar: Department of Physics, Professor T.T.S. Kuo, State University of New York at Stony Brook, ENERGY-INDEPENDENT OPTICAL MODEL POTENTIALS.

December 10, 1981

Solid State Seminar: Department of Physics, Dr. Priya Vashishta, Argonne National Laboratory, STRUCTURAL TRANSITIONS AND HOMOGENEOUS NUCLEATION IN SUPERIONIC CONDUCTORS.

December 14, 1981

Solid Mechanics Seminar: Division of Engineering, Professor Maria Comninou, University of Michigan, CRACK AND CONTACT PROBLEMS WITH FRICTION.

December 14, 1981

Physic Colloquium: Department of Physics, Professor J. Berlinsky, University of British Columbia and M.I.T., ATOMIC HYDROGEN AT LOW TEMPERATURES.

December 15, 1981

Solid Mechanics Seminar: Division of Engineering, Professor Jim Barber, University of Michigan, THERMOELASTIC CONTACT PROBLEMS.

December 15, 1981

Chemistry Colloquium: Department of Chemistry, Dr. Daniel McDonald, University of Chicago, ROTATIONAL DIFFUSION: OPTICALLY INDUCED TRANSIENT MOLECULAR BIREFRINGENCE AND DICHROISM.

December 17, 1981

Special Solid State Seminar: Department of Physics, Dr. Anil Khurana, Universitat Heidelberg, REPLICA SYMMETRY AND DYNAMICAL RESPONSE IN THE SHERRINGTON KIRKPATRICK MODEL OF A SPIN GLASS.

January 11, 1982

Physics Colloquium: Department of Physics, Dr. M. Cage, National Bureau of Standards, DETERMINATION OF THE FINE-STRUCTURE CONSTANT AND A RESISTANCE STANDARD BASED ON THE QUANTIZED HALL EFFECT.

January 18, 1982

Solid Mechanics Seminar: Division of Engineering, Mr. Mark M. Little, Rensselaer Polytechnic Institute, TIME-DEPENDENT PLASTICITY -- SOME IMPLICATIONS FOR FRACTURE.

January 18, 1982

Chemistry Colloquium: Department of Chemistry, Dr. Gregory Ezra, University of Chicago, INTERPARTICLE CORRELATIONS IN 3 BODY SYSTEMS OR THE MOLECULAR STRUCTURE OF THE HELIUM ATOM.

January 20, 1982

Chemistry Colloquium: Department of Chemistry, Dr. Warren Warren, California Institute of Technology, PHASE COHERENCE IN MULTIPLE PHASE SPECTROSCOPY.

January 21, 1982

Condensed Matter Seminar: Department of Physics, Dr. Jack Rowe, Bell Laboratories, RECENT STRUCTURAL STUDIES OF SURFACES USING EXAFS.

January 22, 1982

Chemistry Colloquium: Department of Chemistry, Dr. James L. Kinsey, Massachusetts Institute of Technology, STIMULATED EMISSION PUMPING: AN "EASY ROUTE" TO HIGHLY EXCITED VIBRATIONAL LEVELS OF POLYATOMIC MOLECULES.

January 25, 1982

Solid Mechanics Seminar: Division of Engineering, Professor Alain Molinari, University of Metz, TRANSIENT WAVES IN DISSIPATIVE MATERIALS.

January 28, 1982

Condensed Matter Seminar: Department of Physics, Dr. W.F. Egelhoff, Jr., National Bureau of Standards, SURFACE CORE LEVEL SHIFTS IN BINARY ALLOYS: ΔH OF SURFACE SEGREGATION AND CHEMISORPTION.

February 1, 1982

Solid Mechanics Seminar: Division of Engineering, Dr. George Green, G.E. Research Labs, EVIDENCE FOR CRACK TIP CONTROLLED STABLE CRACK GROWTH.

February 4, 1982

Condensed Matter Seminar: Department of Physics, Dr. B. Berry, IBM, METALLIC GLASSES.

February 5, 1982

Chemistry Colloquium: Department of Chemistry, Dr. Tom George, University of Rochester, LASER INDUCED MOLECULAR RATE PROCESSES IN THE GAS PHASE AND AT A SOLID SURFACE.

February 8, 1982

Solid Mechanics Seminar: Division of Engineering, Professor John W. Hutchinson, Harvard University, TRANSFORMATION TOUGHENING IN CERAMICS.

February 11, 1982

Condensed Matter Seminar: Department of Physics, Professor W. Unertl, University of Maine--Orono, SURFACE STUDIES USING HIGH ENERGY IONS.

February 15, 1982

Physics Colloquium: Department of Physics, Dr. V.J. Emery, Brookhaven National Laboratory, ORGANIC SUPERCONDUCTORS.

February 18, 1982

Condensed Matter Seminar: Department of Physics, Dr. H. Sompolinsky, Harvard University, THE SPIN GLASS PHASE: ORDER ON A HIERARCHY OF TIME SCALES.

March 1, 1982

Solid Mechanics Seminar: Division of Engineering, Professor Ricci Raj, Cornell University, SOLUTION PRECIPITATION CREEP.

March 2, 1982

Chemistry Colloquium: Department of Chemistry, Dr. Lynn Jelinsky, Bell Laboratories, SOLID STATE NMR OF ORGANIC MATERIALS.

March 3, 1982

Special Theoretical Seminar: Department of Physics,
Professor D. Weingarten, Indiana University, NEW RESULTS
IN MONTE CARLO CALCULATIONS WITH FERMIONS.

March 4, 1982

Condensed Matter Seminar: Department of Physics, Dr. E.
Pytte, IBM, THEORY AND EXPERIMENT ON THE RANDOM-FIELD
ISING MODEL.

March 8, 1982

Solid Mechanics Seminar: Division of Engineering,
Professor Alicja Golebiewska Herrmann, Stanford
University, THE USE OF PATH INDEPENDENT INTEGRALS FOR
PLANE CRACK PROBLEMS.

March 10, 1982

Solid Mechanics Seminar: Division of Applied
Mathematics, Professor H. Kirchner, Massachusetts
Institute of Technology, PLASTIC DEFORMATION OF BODY
CENTERED METALS.

March 15, 1982

Solid Mechanics Seminar: Division of Engineering,
Professor John Bassani, University of Pennsylvania,
CRACKS IN MATERIALS WITH HYPERBOLIC SINE LAW CREEP.

March 16, 1982

Solid Mechanics Seminar: Division of Applied
Mathematics, Professor Fikry R. Botros, Columbia
University, CREEP BUCKLING OF STRUCTURES.

March 19, 1982

Condensed Matter Seminar: Department of Physics,
Professor M. Stephens, Rutgers University, HOPPING
CONDUCTIVITY IN ONE DIMENSION.

March 22, 1982

Solid Mechanics Seminar: Division of Engineering,
Professor Xanthippi Markenshoff, University of
California -- Santa Barbara, NON-UNIFORM MOTION OF AN
EDGE DISLOCATION IN AN ANISOTROPIC MEDIUM.

March 22, 1982

Physics Colloquium: Department of Physics, Professor

John J. Quinn, Brown University, SOME ELECTRONIC PROPERTIES OF TWO-DIMENSIONAL SYSTEMS.

March 25, 1982

Condensed Matter Seminar: Department of Physics, Dr. Ron Pindak, Bell Laboratories, VARIABLE DIMENSIONALITY AND NOVEL STRUCTURAL ORDER IN LIQUID CRYSTAL FILMS.

March 29, 1982

Solid Mechanics Seminar: Division of Engineering, Dr. Lawrence M. Brown, F.R.S., Cambridge University, MICRO-MECHANISMS IN FATIGUE.

March 29, 1982

Physics Colloquium: Department of Physics, Professor Robert J. Birgeneau, Massachusetts Institute of Technology, SYNCHROTRON STUDIES OF MELTING IN TWO DIMENSIONS.

April 1, 1982

Condensed Matter Seminar: Department of Physics, Professor R. A. Pelcovits, Brown University, PHONON TRANSMISSION ACROSS THE SOLID-LIQUID HELIUM INTERFACE.

April 9, 1982

Special Theoretical Seminar: Department of Physics, Dr. David Campbell, Los Alamos National Laboratory, POLYACETYLENE.

April 16, 1982

Chemistry Colloquium: Department of Chemistry, Dr. Jeffrey Schwartz, Princeton University, ALKYLIDENE-BRIDGED HETEROBIMETALLIC COMPLEXES: NEW WITTIG-TYPE REAGENTS.

April 19, 1982

Physics Colloquium: Department of Physics, Professor William Risen, Jr., Brown University, RAMAN SPECTROSCOPY AND RECENT APPLICATIONS IN MATERIALS SCIENCE.

April 21, 1982

Condensed Matter Seminar: Department of Physics, Professor E. Burstein, University of Pennsylvania, RESONANT RAMAN SCATTERING AND LUMINESCENCE BY MOLECULES ON "SMOOTH" METAL SURFACES.

April 22, 1982

Joint Electrical Engineering and Condensed Matter Seminar: Department of Physics, Dr. Tom Tiedge, Exxon Research and Engineering Company, DISPERSIVE CHARGE TRANSPORT IN A-Si:H.

April 26, 1982

Physics Colloquium: Department of Physics, Dr. P.C. Schultz, Corning Glass, EXPLORATORY RESEARCH ON HIGHLY TRANSPARENT MATERIALS.

April 27, 1982

Special Condensed Matter Seminar: Department of Physics, Professor D. Goodstein, California Institute of Technology, PHONON-INDUCED DESORPTION OF THE ATOMS.

April 28, 1982

Materials Science Seminar: Materials Research Laboratory, Dr. Ron Stoltz, Exxon Research Laboratory, CURRENT RESEARCH INTERESTS IN MICROMECHANICS OF DEFORMATION AND FRACTURE AT EXXON.

April 29, 1982

Ph.D. Expository Talk: Division of Applied Mathematics, William Hrusa, GLOBAL EXISTENCE OF SMOOTH SOLUTIONS TO THE EQUATIONS OF MOTION FOR MATERIALS WITH FADING MEMORY.

April 29, 1982

Theoretical Seminar: Department of Physics, Professor M. Peskin, Cornell University, A SUBGROUP ALIGNMENT PARADOX IN TWO DIMENSIONS.

April 30, 1982

Chemistry Colloquium: Department of Chemistry, Dr. Milton Cole, Pennsylvania State University, IS THERE A UNIVERSAL LAW OF PHYSICAL ADSORPTION?

May 5, 1982

Solid Mechanics Seminar: Division of Applied Mathematics, Dr. M.F. Kanninen, Battelle Columbus Laboratories, ELASTIC-PLASTIC FRACTURE MECHANICS SIMULATIONS OF SUB-CRITICAL CRACK GROWTH IN WELD-INDUCED RESIDUAL STRESS AND DEFORMATION FIELDS.

May 6, 1982

Condensed Matter Seminar: Department of Physics, Professor Victor E. Henrich, Yale University, ELECTRON SPECTROSCOPIC STUDIES OF OXIDE SURFACES: ELECTRON STRUCTURE, DEFECTS, AND CHEMISORPTION.

May 7, 1982

Joint Electrical Sciences - Solid State Seminar: Division of Engineering, Professor Fred Davidson, The Johns Hopkins University, PHOTO-RESPONSE CHARACTERISTICS OF NICKLE-NICKLE OXIDE-NICKLE THIN FILM TUNNELING JUNCTIONS.

May 7, 1982

Senior Physics Honor Seminar: Department of Physics, Eric Kronenberg, Brown University, SELF-CONSISTENT PHONON THEORY OF STRUCTURAL PHASE TRANSITION.

May 17, 1982

Solid Mechanics Seminar: Division of Engineering, Professor E.H. Lee, Rensselaer Polytechnic Institute, STRESS ANALYSIS FOR KINEMATIC HARDENING IN FINITE-DEFORMATION PLASTICITY.

May 18, 1982

Special Physics Colloquium: Department of Physics, Professor P. de Gennes, College de France, THE PHYSICS OF ENTANGLED POLYMERS.

May 19, 1982

Surface Science Seminar: Department of Physics, Professor Milton Cole, Pennsylvania State and Brown Universities, STICKING, DESORPTION, DIFFUSION AND ALL ON SOLID SURFACES.

May 19, 1982

Special Physics Colloquium: Department of Physics, Professor A. W. Overhauser, Purdue University, THE MYSTERIES OF SIMPLE METALS.

May 20, 1982

Lefschetz Center for Dynamical Systems Seminar: Division of Applied Mathematics, Professor Harris McClamroch, University of Michigan, CONTROL OF ELASTIC STRUCTURES: APPLICATION TO A PROBLEM IN CIVIL ENGINEERING.

May 28, 1982

Surface Science Seminar: Department of Physics, Anne
Horlacher, Brown University, HYDROGEN ON W(001):
DESORPTION AND STRUCTURE.

List of Staff in the Materials Research Laboratory Program

APPLIED MATHEMATICS

NAME	TITLE
C. Elbaum	Professor (Physics)
H. Kolsky	Professor (Engineering) (Physics)
A.C. Pipkin	Professor
A. Hikata	Professor (Research)
G. Sun	Visiting Research Associate
W. Carey	Technical Assistant
P. Russo	Technical Assistant

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K. Kim	Assistant Professor (Research)
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J. Covino	Research Assistant
J. Erickson	Research Assistant
J. Foise	Research Assistant
J.S. Hayden	Research Assistant
A. Horlacher	Research Assistant
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J. Keeley	Research Assistant
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H. Leiva	Research Assistant
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J. Prybyla	Research Assistant
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A. Molinari	Visiting Assistant Professor
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J. Ajo	Research Assistant
R. Arya	Research Assistant
C. Case	Research Assistant
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R. Deshmukh	Research Assistant
G. Doodlesack	Research Assistant
A.S. Douglas	Research Assistant

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NAME	TITLE
J. Beamish	Research Associate
A.M.M. Pruisken	Research Associate
L. Roelofs	Research Associate

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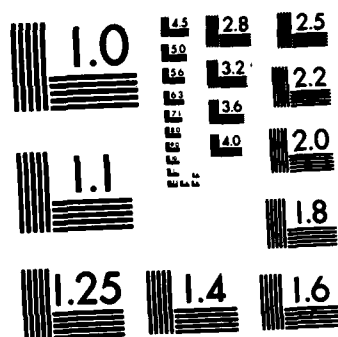


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List of Staff in the Materials Research Laboratory Program

PHYSICS

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P.J. Bray	Professor
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A. Houghton	Professor
H. Kolsky	Professor (Applied Mathematics) (Engineering)
J.M. Kosterlitz	Professor
H.J. Maris	Professor
J.J. Quinn	Professor
G.M. Seidel	Professor
P.J. Stiles	Professor
J. Tauc	Professor (Engineering)
S-C. Ying	Professor
R.A. Pelcovits	Assistant Professor
F. Bucholtz	Research Assistant
J.W. Chung	Research Assistant
G. Cibuzar	Research Assistant
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S.J. Gravina	Research Assistant
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T. Huber	Research Assistant
J. Lee	Research Assistant
A.D. LeGrand	Research Assistant
M.L. Lui	Research Assistant
M. Manning	Research Assistant
R. Mayer	Research Assistant
R. Mulkern	Research Assistant
B.D. Parker (Fellow)	Research Assistant
D. Pfof	Research Assistant
S. Ray	Research Assistant
J.R. Senna	Research Assistant
F. Seco	Research Assistant
R.P. Smith	Research Assistant
J. Strait	Research Assistant
D.A. Syphers	Research Assistant
E. Vera	Research Assistant

M. Williams
J.L. Wilson
K.S. Yi

Research Assistant
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